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PRODUCTION OF CLEAN FUEL GAS FROM BITUMINOUS COAL

Consolidation Coal Company

PREPARED FOR
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December 1973

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The report describes the initial experimental study of a process for producing clean low-Btu fuel gas from caking bituminous coals. The process consists of a sequence of coal-processing steps--coal pretreatment, gasification of the pretreated material, and combustion of the residual char to provide process heat--followed by desulfurization of the resulting gas at high temperature and pressure. A fluidized bed of half-calcined dolomite is used for desulfurization. Partially sulfided sorbent is regenerated using steam and CO_2, and elemental sulfur is recovered from the regenerator off-gases using a liquid-phase Claus process. Most process steps have been experimentally investigated, and an economic evaluation has been conducted. The gas could be utilized to generate electricity with low environmental impact, employing an advanced power cycle (or a conventional power boiler).

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PRODUCTION OF CLEAN FUEL GAS FROM BITUMINOUS COAL

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ABSTRACT

A process for the production of low-Btu gas from bituminous coals via fluid bed gasification is described. Coal processing consists of pretreatment, gasification, and final burnup. Hot fuel gas is desulfurized with half-calcined dolomite and cleaned of particulates in high-pressure drop cyclones. The sulfur acceptor is regenerated with steam and CO_2. A liquid-phase Claus reactor is used to process the H_2S in the regenerator offgas into elemental sulfur.

Experimental data are presented which demonstrated feasibility of the major process steps: pretreatment, gasification, carbon burnup, desulfurization, regeneration, and liquid-phase Claus processing. In all cases, however, more experimental data are required to optimize conditions.

An economic evaluation of gas clean-up operations shows that regenerative use of acceptor is preferable to once-through, and that removal of particulates via cyclones, if feasible, is cheaper than water scrubbing with subsequent reheat. The cost of the gas desulfurization process including sorbent regeneration and sulfur recovery is of the order of 20¢/MM Btu of product gas.

This report was submitted in partial fulfillment of Contract No. EHSD 71-15 under the sponsorship of the Demonstration Projects Branch, Control Systems Laboratory, Office of Research and Development of the Environmental Protection Agency. The work was done during the period March, 1972 to June, 1973.

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I. SUMMARY

A. Process Description

The process investigated is illustrated in Figure 1. The basic flow sheet represents a revision of the original process investigated in the first year of the EPA Contract EHSD 71-15 as reported in detail in the Annual Report.(1) The revised process separates the sulfur removal from the gasification steps of the process. Hot sulfur removal is effected in a fluid bed by means of half-calcined dolomite utilizing the reaction,

$$H_2S + CaCO_3 = CaS + H_2O + CO_2$$

at ca. 1650°F.

The gasification section now no longer utilizes CO_2 acceptor action as a source of heat. Efficient carbon utilization is now effected by use of a two-stage fluid bed, air-blown gas producer wherein the second stage performs the function of a carbon burn-up cell.

B. Pretreatment

Two aspects of pretreatment for highly fluid Pittsburgh Seam coals were studied experimentally. The first was an extension of previous work using preoxidation to render these coals noncaking in the process. The prior work had demonstrated that an excessive level of preoxidation compared to the adiabatic level was required. The use of two stages of preoxidation, with a rising temperature between stages, and of finer size consist of coal was investigated. Both of these expedients favor reduction of the level of preoxidation required. The combination of both did not, however, permit reduction of the preoxidation to the adiabatic level.

The second phase of the pretreatment work explored the concept of the Seeded Coal Process wherein the fluidity of the coal is utilized to produce a dense noncaking gasifier feed. Coal and seed char would be fed into a draft tube in a fluidized bed at 1000-1400°F. The coal melts, smears out over the surface of the char and then solidifies on the completion of pyrolysis. Initial results were encouraging, but larger equipment will be needed to develop the process further.

C. Acceptor Sulfur Cycle Studies

A number of acceptors were studied. A pure Nebraska limestone showed little activity with excellent attrition resistance. An impure limestone, 1691, gave intermediate activity and good attrition resistance, but tended to form agglomerates. All four dolomites showed good activity toward H_2S. H_2S concentration exiting the desulfurizer was usually less than 5% of the inlet and about twice the equilibrium concentration with only an 18-inch bed.

However, of the four dolomites, three showed excessive rates of attrition, 5-10% of the feed per cycle. The fourth dolomite, Canaan stone, showed good activity with an attrition rate of less than 1% per pass.

All stones gave incomplete regeneration, the level of CaS in the acceptor increasing as it was cycled. In the best run, 13% of the total calcium was being converted per pass through the regenerator from CaS to $CaCO_3$. The longest run was for 17 cycles at about 8% conversion per cycle, and there was little decline of activity between the eighth and last cycle.

Tests made with once-through operation showed that the dolomite could achieve a calcium utilization of about 90% with good removal of H_2S in this mode of operation.

D. Carbon Burn-up Cell and Gasifier Demonstration Runs

Several runs explored the effects of temperature and bed expansion on carbon burnout and ash slagging in the carbon burn-up cell. Total carbon utilization was obtained at temperatures as low as 1700°F. At 1900°F, the reactor was run with no evidence of ash slagging at bed expansions of about 60% above the incipiently fluidized bed height.

Operation of the gasifier at process flows and 1725°F was demonstrated with freedom from ash slagging. However, at 1775°F, some mild slagging of the ash occurred. Possibly, operation of the gasifier at a higher bed expansion would lead to successful operation at higher temperatures.

E. Gasification Kinetics

A total of 24 runs were made with char from Pittsburgh Seam coal at 30% and 60% carbon burnoff and at 1620 and 1700°F.

The original process estimates assumed a gasification rate for bituminous coal char equal to 1/15 the rate predicted from our earlier studies on kinetics of lignite char gasification. The current study shows that the assumed rates are too high, mainly because inhibition of the reactions by H_2, relative to inhibition by CO, is greater for the bituminous coal char.

The quantitative effect on the process has not been evaluated. Qualitatively more steam will be needed in the gasifier and the thermal efficiency will decrease somewhat.

F. Liquid-Phase Claus Process

The liquid-phase Claus reaction, using only water as the liquid, was found to proceed readily under process conditions. The product liquor contained 0.1% or less soluble sulfur. Continued recycle caused no increase in soluble sulfur or total acidity.

The scope of the effort was insufficient to fully elucidate the behavior of the system with respect to reactor volume and gas concentration. Preliminary indications are that the system is between first and second order with respect to both.

Conversion of over 90% of the feed H_2S-SO_2 was obtained using a reactor volume consistent with process estimates.

G. Feasibility Study

The economic feasibility study was limited to consideration of high temperature (1650°F) desulfurization of pressurized producer gas as fed to a power station using half-calcined dolomite as the sorbent. Two methods were compared for cleanup of particulates and alkali, i.e., hot cyclones only and wet scrubbing with gas reheat. The economic comparison is summarized in Table 3 in Section III of the report dealing with the feasibility study.

The hot cyclone method of gas cleanup gave an advantage equivalent to about one dollar per ton of feed coal. The investment cost of the plant facilities for desulfurization of the producer gas, regeneration of the sorbent and recovery of elemental sulfur was $32.00 per installed KW. The processing cost was estimated as 20¢/MM Btu of product gas. The basis for the economic evaluation was 1978 operation at 70% load factor; 7.5% escalation, interest during construction, and interest on working capital; and 18% capital charge.

The "once-through" case wherein the sorbent is not regenerated was also examined. This alternative was deemed uneconomical because of the high cost of make-up stone and for treatment and disposal of the spent stone.

II. CONCLUSIONS AND RECOMMENDATIONS

A. Overall Process

The last Annual Report(1) examined the low Btu gasification process integrated with advanced power cycles and concluded that the process had economic merit. This report deals with a revised gasification system (cf. Figure 1) using a separate hot removal of H_2S from the producer gas with half-calcined dolomite (i.e., $MgO \cdot CaCO_3$). The economic study given in this report is, however, limited to consideration of the gas desulfurization and clean-up system. The previous conclusion,(1) that after hot desulfurization, the hot removal of particulates and alkali is better than wet particulate scrubbing with subsequent gas reheat within the context of the revised process, was confirmed. In addition, the regenerative process was shown to be cheaper than once-through processing. Further economic studies should be carried out, however, to determine whether the hot gas desulfurization process is also cheaper than conventional wet H_2S removal.

It is recommended that low Btu gas process research and development be continued. The cleanup of the fuel gas should use a regenerative process for desulfurization with a hot system for removal of particulates and alkali. The next phase of the work should concentrate on development of the hot gas clean-up system independently of the specific gasification process used. The specific gasification system described in this report, however, also has merit and consideration should also be given to its further development. Recommendations follow with respect to further work needed on the specific process steps of the gasification and sulfur removal and recovery system.

B. Pretreatment

The pretreatment technique with the most potential is the Seeded Coal Process which produces a dense, operable gasifier feedstock. Further work should be carried out in a larger processing unit, so that the particle Reynolds numbers will be well into the turbulent regime thereby giving good mixing of feed coal and char. A unit processing about 300 lb/hr is envisaged.

Earlier work indicated that preoxidation was a viable (within the constraints of adiabatic operation) pretreatment technique for Illinois No. 6 coal but not for Pittsburgh Seam coals. Further work remains to be done to determine how much further reduction in required preoxidation for Pittsburgh Seam coals can be effected by optimization of the process. An increasing number of stages of preoxidation, i.e., from two to three, and the use of an optimum temperature for each stage (rising temperature regime) can significantly reduce the level of preoxidation. Similarly, the effect of the use of a higher partial pressure of oxygen approaching the design condition of 3 atmospheres inlet partial pressure in reducing the level of preoxidation should be investigated.

C. Gasification and Carbon Burnup

Demonstration of operability of these reactors at process conditions was carried out. Further work on operability characteristics and reaction rates in the above vessels should be carried out. It would be particularly desirable from the kinetic point of view to determine operating conditions in the gasifier

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under which the presently proven operable temperature could be increased significantly above 1725°F. Additional gasification kinetics data and associated correlation work would be desirable to permit more reliable design of the gasification system.

D. Acceptor Sulfur Cycle

Additional data on the acceptor sulfur cycle are still needed to more adequately define acceptor make-up requirements. The acceptor life as a function of conditions in each reaction vessel, gas desulfurizer and regenerator, remain to be defined. Approach to equilibrium in the gas desulfurizer with acceptor that has undergone numerous cycles has yet to be demonstrated. In the current work, the later cycles were conducted with H_2S breakthrough in the gas desulfurizer. This is not necessarily a process restriction but may be attributed to the fact that the circulation rate was not high enough to supply enough $CaCO_3$ to the gas desulfurizer for efficient H_2S absorption.

The prospects for finding widely distributed acceptors with good activity and attrition resistance remain to be examined. A program for hardening even soft dolomites should be initiated. Fortunately, as discussed in the feasibility study, acceptor costs are small for the regenerative case, and fairly high shipping costs can be absorbed.

E. Hot Particulate Removal

Further work remains to be done to demonstrate hot removal of particulates and alkalis. An "optimum" system would be one wherein both H_2S and particulates are simultaneously removed. Such a study would have to be carried out on larger scale equipment than used in the present work.

F. Liquid-Phase Claus Reaction

Feasibility of the process step was proven during the current contract period. Further work is needed to define the optimum system with respect to reactor volume, gas concentration, temperature and mixing or agitation.

In addition, there are rich possibilities for improvements via the addition of catalysts and buffers. The area of nonaqueous solvents also remains to be explored. While the process is workable as is, considerable improvements may be attainable.

G. Chance Reaction - Disposal of Spent Acceptor

Spent acceptor contains $MgO \cdot CaS$ which cannot be disposed of without further treatment to change CaS back to $CaCO_3$. The Chance reaction was carried out commercially in the 19th century to dispose of the same nuisance CaS. While data are expected to accrue from the Chance reactor installed at Consol's Rapid City gasification plant, research will be needed to define the best mode of operation for the low Btu gasification process. In particular, the fate of the magnesium and the reactivity of unregenerable CaS in an aqueous medium should be studied.

H. Pilot Plant Design

The speed with which this process will be commercialized is a function of the dollar input to its development. Sufficient data are on hand to design the front end of a pilot plant comprising preoxidative pretreatment, a gasifier and a burn-up cell. Presumably, sufficient data will be on hand within a year for design of the desulfurization and sulfur recovery system.

An alternate scheme would be to adapt the hot desulfurization process described herein to an existing gasification unit such as one using the Lurgi process.

III. FEASIBILITY STUDY

A. Introduction

The production of low-sulfur producer gas via an adaptation of the CO_2 Acceptor Process formed the subject matter that was studied under the first year of the EPA Contract EHSD 71-15.

A detailed process design and feasibility study of the system as well as an experimental evaluation was carried out. The results are reported in the Annual Report.(1)

The experimental evaluation of the system indicated feasibility of all steps in the process with one exception. It was found that the sulfur recovery from the acceptor would be incomplete from the regenerator in the Case I scheme of that report. This necessitated addition of another step in the process in which sulfur was rejected by the reaction,

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S,$$

as shown for Case II in the Annual Report.(1) With this added complication introduced, further thought was given to refining and simplifying the overall process.

It became apparent that there is no real advantage in using the CO_2 acceptor reaction simultaneously with the sulfur acceptor reaction in the gasifier when low-Btu fuel gas is the desired product. The gasification system was revised to provide for disposition of the residual char by use of a carbon burn-up cell which preheats all the steam and air required for the gasifier. The sensible heat duty involved in preheating serves as the "heat sink" which is necessary to prevent ash slagging during combustion of the residual gasifier char. In the CO_2 Acceptor Process the heat sink is provided by the endothermic calcining reaction in the acceptor regenerator.

Since the acceptor no longer needs to be in the gasifier, desulfurization is now carried out as a separate operation. The sulfur acceptance reaction is conducted in a dense-phase fluidized bed of dolomite to which the acceptor is fed in the form of $MgO \cdot CaCO_3$. The feasibility study presented here provides the basic process design parameters for both the gasification and sulfur removal systems. The economics, however, are limited to the sulfur removal and recovery systems.

B. Overall Process Description

A schematic diagram of the revised process is shown in Figure 1. The hot fuel gas is desulfurized in the H_2S sorption bed by the reaction,

$$H_2S + CaCO_3 = CaS + H_2O + CO_2.$$

The bed temperature is held at a level below which the acceptor can calcine by the reaction,

$$CaCO_3 = CaO + CO_2.$$

The low-sulfur hot gas is cooled to 1300°F by heat exchange with the water needed to generate the gasifier steam, and then is cleaned of particulates and alkali by high pressure drop cyclones.

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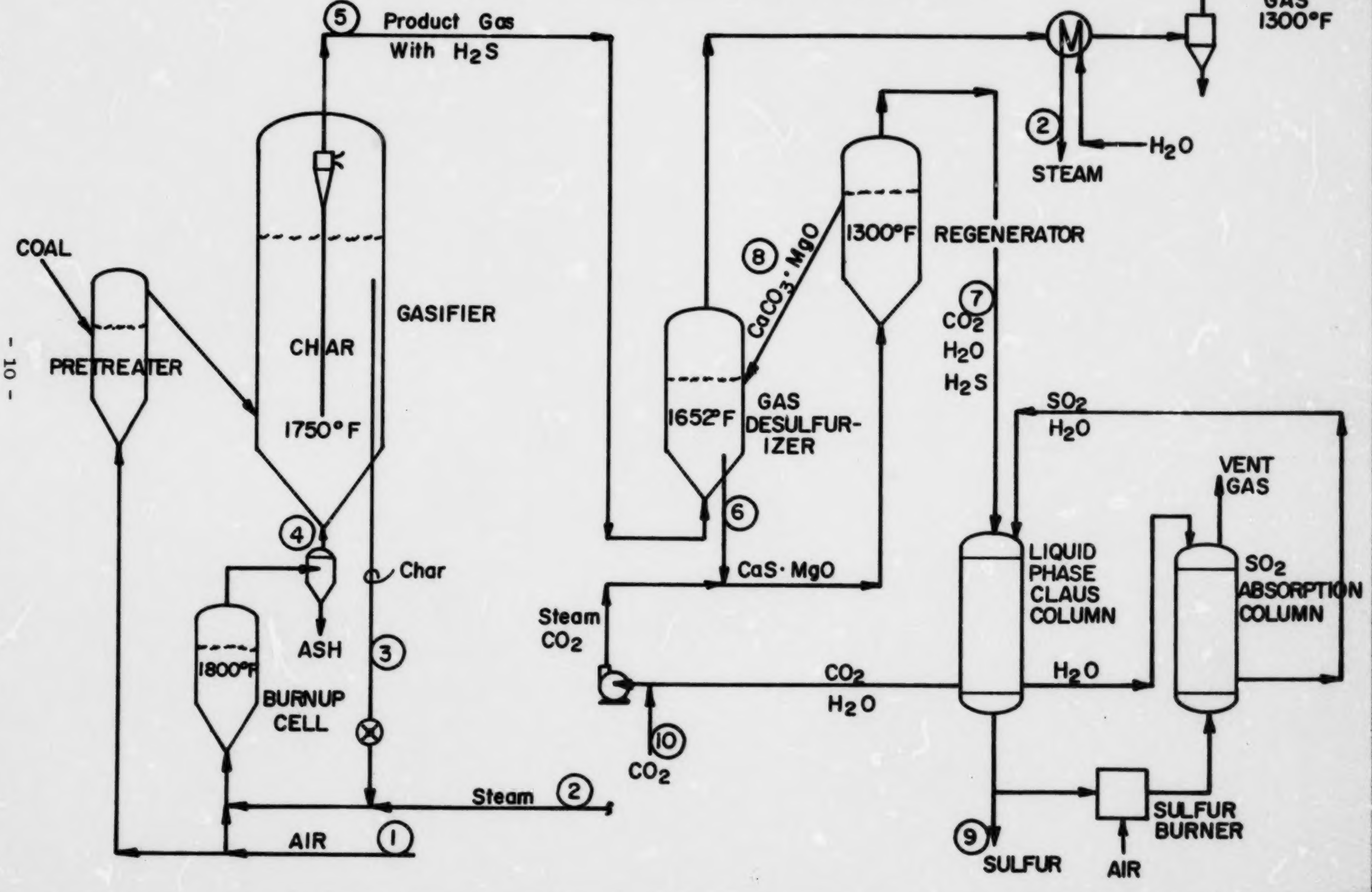
Figure I

TWO STAGE FLUIDIZED BED
PARTIAL COMBUSTION PROCESS



COAL
PRETREATER
CHAR
1750° F
GASIFIER
⑤ Product Gas
With H_2S
④
ASH
Char
③
1800°F
BURNUP
CELL
AIR ①
Steam ②
1652°F
GAS
DESULFUR-
IZER
⑥
CaS · MgO
Steam
CO_2
⑩
CO_2
CO_2
H_2O
⑧
$CaCO_3 \cdot MgO$
1300°F
REGENERATOR
⑦
CO_2
H_2O
H_2S
SO_2
H_2O
LIQUID
PHASE
CLAUS
COLUMN
H_2O
⑨
SULFUR
SULFUR
BURNER
AIR
VENT
GAS
SO_2
ABSORPTION
COLUMN
②
STEAM
H_2O
⑪
CLEAN
PRODUCT
GAS
1300°F

The sulfided acceptor is conveyed to the regenerator by continuously recirculating a stream of CO_2 and steam. In the regenerator the reverse of the H_2S sorption reaction takes place at 1300°F.

$$CaS + CO_2 + H_2O = CaCO_3 + H_2S.$$

The regenerated acceptor is returned by gravity to the sorption reactor.

A computer program has been devised to evaluate the heat and material balance relationships and overall thermal efficiency of the scheme as shown in Figure 1, and accordingly, includes both the gasification and gas desulfurization sections of the process.

The program evaluates the interaction among the various components of the system consistent with the thermodynamic, fluo-solids mechanics and kinetic restraints on the system.

The entire system was represented by 27 simultaneous linear and non-linear equations which represent the five basic process steps given below:

1. Carbon burn-up cell.
2. Gasifier.
3. Gas desulfurizer.
4. Steam-product gas exchanger.
5. Regeneration reaction - impact of temperature only.

which also are interrelated by the following quantities:

1. H, C, O balance.
2. Heat balances around components 1 through 4, above.
3. Water-gas-shift equilibrium in components 2 and 3, above.
4. Methane yield correlation.
5. Equilibrium in the reaction,

$$CaCO_3 + H_2S = CaS + CO_2 + H_2O.$$

The above equations were solved by an iterative procedure for the mols of air and steam fed to the burn-up cell as a function of the following:

1. Burn-up cell temperature.
2. Gasifier temperature.
3. CaS/total calcium, mol ratio in sorbent.
4. Regenerator temperature.

Once having computed the input and output flows and compositions by the method outlined above, it was necessary to determine the gasification reactor sizes. The vessel sizing is determined by the interaction of the fluidization mechanics of the char particles and the gasification kinetics.

The basis used here was to process 120,800 lb/hr of coal through each pretreater-gasifier. The fluidized bed height was fixed at 50 feet. The fluidized bed density was then calculated using the correlation developed during the work on the CO_2 Acceptor Process.(2) It was assumed here that a high density closely sized char particle would be generated by the "Seeded Coal Process" from Ireland Mine coal, i.e., the mean particle diameter was taken as 0.04 inch and the initial particle density as 85 lb/ft^3. The reduction in particle density as affected by carbon burnoff was based on the relationships developed during the work on the CO_2 Acceptor Process.(3)

It is now necessary to compute the vessel cross section and fluidizing velocities which are compatible with the estimated bed inventories by use of reaction kinetic data.

Extensive differential rate data(4,5,6) were obtained some time ago on the gasification of bituminous coal chars as a function of temperature, pressure and mol fraction of hydrogen in hydrogen-steam mixtures. Subsequently, extensive kinetic data were obtained also on the gasification kinetics of lignite char.(3,7) In that work it was found that the reaction rate was strongly inhibited by the presence of CO as well as hydrogen. Thus, the prior data on bituminous coal chars could not be used in practice since the inhibiting effect of CO was not taken into account. However, under comparable conditions, i.e., in the absence of CO, it was found that on the average the bituminous coal chars had about 1/15th the reactivity of the lignite chars.

Therefore, in developing the kinetic calculations the equations developed for lignite char(7) were used with introduction of a correlation factor of 1/15th to account for the lower reactivity of the bituminous coal chars. The differential kinetics were translated into integral kinetics, i.e., average over the whole bed by the method given in Appendix D of the Annual Report.(1)

Having calculated the integral rate R_T, the required bed inventory is calculated from the equation,

$$R_T = \frac{\text{lb Fixed Carbon Gasified}}{\text{min/lb Fixed Carbon in Bed}} \times 10^{-4}$$

The fluidization calculations outlined above are then used to determine the required vessel cross section and fluidizing velocity.

A total of fifteen cases were computed covering gasification temperatures between 1650 and 1750°F. Because of the kinetic and thermodynamic limits, the system is highly constrained, and the response of the system is quite limited. This is illustrated by the ranges given in Table 1.

The conditions for the base case, which all things considered, is felt to be close to a practical "optimum" for the system, are also given in Table 1. A more complete heat and material balance around the base case is also given in Table 2.

The process concept given here has several potential advantages over the original process which utilized the CO_2 Acceptor Process as outlined below:

Operability may be improved in the new process by virtue of:

1. The O_2 partial pressure to the burn-up cell is lower than to the previous regenerator. Steam and air N_2 serve as the heat sink. There is less chance of ash slagging, especially since the burn-up cell can be operated at much lower temperatures than are needed to calcine $CaCO_3$.

2. The O_2 partial pressure to the gasifier is lower since the air is diluted with all of the input steam and all of the products of combustion of the burn-up cell. Thus, the temperature can be raised to 1750°F as in the base case to improve kinetics without increasing the danger of ash slagging.

Table 1

Range of Variables Studied in System Analysis

Range of Independent Variables Studied		Base Case
Gasifier Temperature, °F	1650-1750	1750
Burn-up Cell Temperature, °F	1750-1950	1800
S/Σ Ca, mol ratio	0.1-0.4	0.13
Regenerator Temperature, °F	1200-1300	1300
Range of Calculated Quantities		
Cold Gas Efficiency, %	79.1-81.2	79.8
HHV Dry Product Gas, Btu/ft^3	143-149	144
% Sulfur Removed	93.1-97.5	97.0
Steam Conversion, %	49.4-55.7	52.9
Carbon to Burn-up Cell, Wt % of C in Coal Feed	13.4-16.9	13.4
Gasification Rate $\frac{\text{lb C (gasified)} \times 10^4}{\text{lb C in Bed, min.}}$	45-88	88
Gasifier Diameter, I.D., ft	24.8-25.3	24.8
Char Particle Density, lb/ft^3	27-36	27
Gas Fluidizing Velocity, ft/sec	1.46-1.55	1.48
Gasifier Cross Section Index*	392-415	395
Constant Parameters		
System Pressure, atm.	← 15 →	
Gas Outlet Temperature, °F	← 1300 →	

* Ft^2/10^9 Btu/hr (HHV of Product Gas).

Table 2

Key Stream Flows and Analyses

Basis: 100 lb dry coal(1)
6% moisture as fed
System Pressure: 15 atm (206 psig)

Stream No.(2)	1	2	3	4	5	6	7	8	9	10	11
Identification	Air	Steam	Fuel Char	Burn-up Cell Gas	Raw Product Gas	Spent Acceptor	"Squires" Offgas	Regenerated Acceptor	Sulfur	CO_2	Clean Product Gas
Temperature, °F	398	780	1750	1800	1750	1652	1300	1300	310	400	1300
Mols	11.70	3.264	.814	12.59	20.50	1.001	3.792	1.001	.1296	.1296	20.63
Pounds			21.73						4.15		
Composition, Mol %											
CH_4				x	1.39		x				1.38
H_2				x	16.23		x				16.51
CO				x	19.42		x				18.91
CO_2				6.19	7.54		63.95				8.51
H_2O	.90			26.93	9.72		32.44				9.90
H_2S				x	.65		3.61				.02
N_2	78.3			57.84	44.80		x				44.52
O_2	20.8			9.04	x		x				x
NH_3					.25						.25
MgO·CaS						88.4		75.4			
$MgO \cdot CaCO_3$						11.6		24.6			
Hydrogen (as H_2)			4.31								
Carbon			95.69								

(1) Ireland Mine Coal:

	Wt. % Dry Basis	Mols
H	4.8	2.381
C	69.8	5.812
N	1.2	--
O	7.6	.475
S	4.3	.1341
Ash	12.3	--

(2) Stream numbers correspond to those shown in Figure 1.

3. More positive contact of dirty gas with the dense-phase bed of acceptor in the gas desulfurizer is effected.

The cold gas efficiency is definitely improved by virtue of:

1. Lower duty to calcine make-up acceptor. Circulation rate is about 1/10th that of the original concept.
2. 100% burn up of carbon (vs. 98%).
3. Improved gasification kinetics require less steam. Thus, there is less latent heat in the product gas.
4. Less air required. Thus, less sensible heat is lost with N_2.

Experimental work was carried out during the contract period covered by this report to evaluate at least in a preliminary manner all of the process steps shown in the schematic diagram of Figure 1. Details of the work are given in the experimental sections of this report.

The feasibility study itself was limited to an economic evaluation of the treatment of the hot producer gas to remove sulfur by means of the dolomite sorbent, the regeneration of the spent sorbent and the conversion of H_2S in the regeneration offgases to elemental sulfur by means of the liquid-phase Claus process.

C. Summary - Gas Purification Costs

Under this contract an economic evaluation of the process is required. The prime purpose of this evaluation is to determine the commercial feasibility of the process, and to delineate those technical areas where further research and development are best directed. The feasibility study is restricted to the cost of desulfurizing the producer gas, including sorbent regeneration and sulfur recovery. The cost of gasification is not included, nor are estimates developed of the cost of generating electric power from the desulfurized producer gas.

The most attractive end use of clean, pressurized, hot producer gas in the long term is in combination with a combined cycle power station. However, since only the gas cleanup end of the plant was evaluated, the commercial evaluation was based on low-sulfur boiler fuel which is a more immediate practical objective. The plant was selected to supply a desulfurized fuel gas to a conventional, gas-burning power station with an approximate rating of 1400 MW. With respect to quantity of gas, this is the same plant size that was considered in the initial feasibility study.(1)

The primary evaluation presented in this study is based on these criteria:

1. Sulfur is removed hot with a regenerable dolomite sorbent.
2. Desulfurized producer gas expanded through a power-recovery turbine before delivery at 10 psig to a power station.
3. Two extremes of further clean up of desulfurized product gas to remove particulates before expansion:
    a. high pressure drop cyclones (or equivalent) only - Case I.
    b. conventional water scrubbing with subsequent gas reheat - Case II.

This evaluation, based on an arbitrary start-up date of January, 1978, is summarized in Table 3.

The cost of the plant facilities to desulfurize producer gas under pressure by this process amount to $32 to $40 per installed KW (1978 cost basis) depending on the mode of subsequent gas cleanup, and the annual operating costs correspond to 1.5 to 1.9 mills/KWH of power generated.

Direct comparison with the economics previously presented in the Annual Report(1) is not possible since the previous study was concerned with the economics of the whole system including the gasifier. The cost of the desulfurization section alone cannot be broken out, since in the former process it was an integral part of the gasifier. The rough magnitude of costs, however, appear to be consistent with each other.

It is clear that there is a significant advantage to be gained from the development of a "hot" gas clean-up technology for alkalis and solids removal (Case I). When compared to the alternative - wet scrubbing with gas reheat (Case II) - the advantage is about $1.00 per ton of feed coal, or 5.3¢/MM Btu of product gas. Over and above the direct cost advantage shown in Table 3 for Case I over Case II, there is also additional excess power available from the expansion of the product gas (about 42 MW equivalent). While it is beyond the scope of this study to evaluate the dollar value of this excess power, it could amount to an additional credit of 0.3-0.6¢/MM Btu of product gas.

A direct comparison of the cost of the "all hot clean-up system" with an "all cold system" including removal of H_2S by wet scrubbing has not been made since it was outside the scope of this study.

The make-up acceptor cost for this evaluation was assumed at a relatively high value of $10 per ton of raw dolomite. The requirements for the regenerative cases are, however, quite modest, and the acceptor cost does not have a significant impact on the desulfurization cost. In this study the rate of make-up acceptor required is estimated as one percent of the circulating acceptor. This is based on a reasonable extrapolation of the laboratory data obtained to date. If the make-up rate were doubled, the desulfurization cost would increase only by 4-5%.

Rather interestingly, the sensible heat content of the desulfurized producer gas delivered to the power station is not an insignificant factor. In a conventional, gas-fired power station, the fuel gas is delivered to the burners at ambient temperature. The combustion air is preheated to 250 to 350°F in an air heater by indirect sensible heat exchange with flue gas. In this process the fuel gas is delivered from the expander to the power station at 540-660°F. If the fuel gas is preheated, then either less air heater surface is required, or more steam can be generated per unit of fuel burned. An exact determination of the dollar value of sensible heat in the fuel gas would require an extensive analysis of the design and cost of the power station proper. This is beyond the scope of this study. However, a reasonable approximation of the value is to credit the system for the sensible heat content of the fuel gas above the temperature of the flue gas exiting the air heater. In this study this temperature is assumed as 300°F. In Table 3, the credit to the process for this excess sensible heat is about 1.0¢/MM Btu or about 5% of the system cost.

Table 3

Summarized Economic Evaluation
Regenerative Acceptor Desulfurization Process

70% Plant Operating Factor (6132 hrs/year)

Case	I	II
Method of Gas Clean-up (Particulate and Alkali)	"Hot" Cyclones only	Wet Scrubbing With Gas Reheat
Coal Required:		
MM Tons/Year (6% Moisture)	← 3,422,000 →	
Higher Heating Value, Btu/Year	← 81.71×10^{12} →	
Producer Gas to Station (After Expansion):		
Mols/Hour	213,700	213,200
Temperature	660°F	540°F
Pressure	10 psig	10 psig
Higher Heating Value, Btu/Year	65.19×10^{12}	64.70×10^{12}
HHV + Sensible Heat Content,(1) Btu/year	68.68×10^{12}	66.99×10^{12}
Desulfurization Plant Investment(2)	$48.3 MM	$59.8 MM
Desulfurization Cost:(2)		
$/Ton Feed Coal	4.03	4.98
¢/MM Btu HHV of Feed Coal	16.9	20.9
¢/MM Btu HHV of Product Gas	21.2	26.4
¢/MM Btu (HHV + Sens. Heat) Product Gas	20.1	25.4
Excess Power Generated by Expander, megawatts(3)	160(4)	118(4)

(1) Sensible heat content above an assumed air heater outlet temperature of 300°F.

(2) January, 1978 operation - includes escalation and interest during construction. Does not include gasification plant cost or the cost of coal.

(3) After deduction of 157 MW required for compression of process air for gasification plant.

(4) Assuming 91% of the isentropic efficiency for the expander, and 89% of the polytropic efficiency for the air compressors (See Reference 8).

While the basic development of this project to date has been devoted to the concept of a regenerable sulfur acceptor, there is some interest in evaluating an alternative process using once-through acceptor. This would result in some simplification of the sulfur recovery system, at the expense of a much greater usage of make-up acceptor, projected to be approximately 15 times the rate of the regenerable acceptor case.

The added make-up acceptor cost for the once-through system (at a make-up acceptor cost of $10 per ton) amounts to about $9,200,000 per year. The maximum saving in plant investment would be $10 MM. At a capital charge of 18%, the annual savings in investment charge is $1,800,000. Make-up acceptor cost exceeds this saving by a five-fold factor.

The maximum savings in the once-through as compared with the regenerative system is limited because of the much greater disposal costs in the former case. A significant cost item here is the necessity to treat the spent stone via the Chance reaction to convert the CaS to $CaCO_3$ before disposal. This step is expensive since 2 mols of CO_2 are required per mol of CaS treated since the MgO is converted to $MgCO_3$ in the process.

It is concluded that there is no economic incentive to further consider the non-regenerative system.

Possibly an alternative disposal method could be developed where spent acceptor could be disposed of as $MgO \cdot CaSO_4$ (e.g., by high-temperature oxidation of $MgO \cdot CaS$). However, our limited data show that the spent CaS is difficult to oxidize and that, during oxidation, some SO_2 inevitably is released which causes an air pollution problem.

D. Process Description - Gas Purification

Introduction

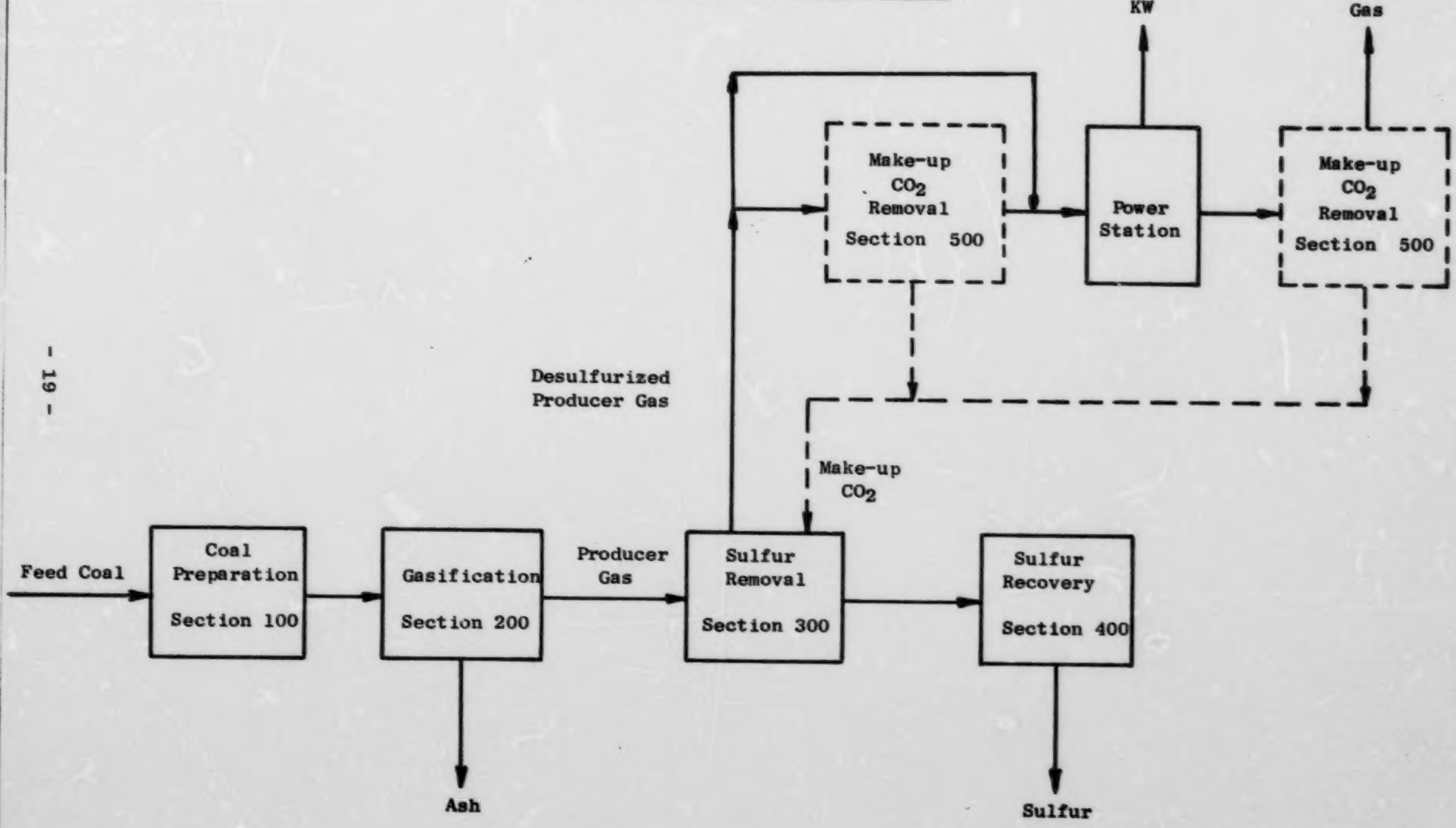
The scope of work under this contract covers the experimental development and economic evaluation of a novel process for desulfurizing pressurized producer gas as a fuel to a power station. The simple block flow diagram in Figure 2 defines the various steps in the overall process. Design and evaluation of coal preparation (crushing and sizing), and of coal gasification (Sections 100 and 200, respectively), are not covered in this study. Section 300, sulfur removal, and Section 400, sulfur recovery, have been completely evaluated and form the substance of this report.

A relatively small quantity of make-up CO_2 is required in the process (Section 500). As shown in Figure 2, the CO_2 could be recovered either from a slip-stream of the desulfurized producer gas before power generation, or from a portion of the power station stack gas. Preliminary cost studies indicate approximately equal costs for the two alternative locations. For the purposes of this study, it is assumed that the make-up CO_2 is recovered from the pressurized producer gas before delivery to the power station. A standard hot potassium carbonate system is assumed to establish capital cost and utility requirements.

There is continued interest in the added cost of wet scrubbing the particulates and reheating the product gas before charging the gas to an expanding turbine-generator set. The equipment required for this additional step is shown in Figure 3 and is identified as Section 600.

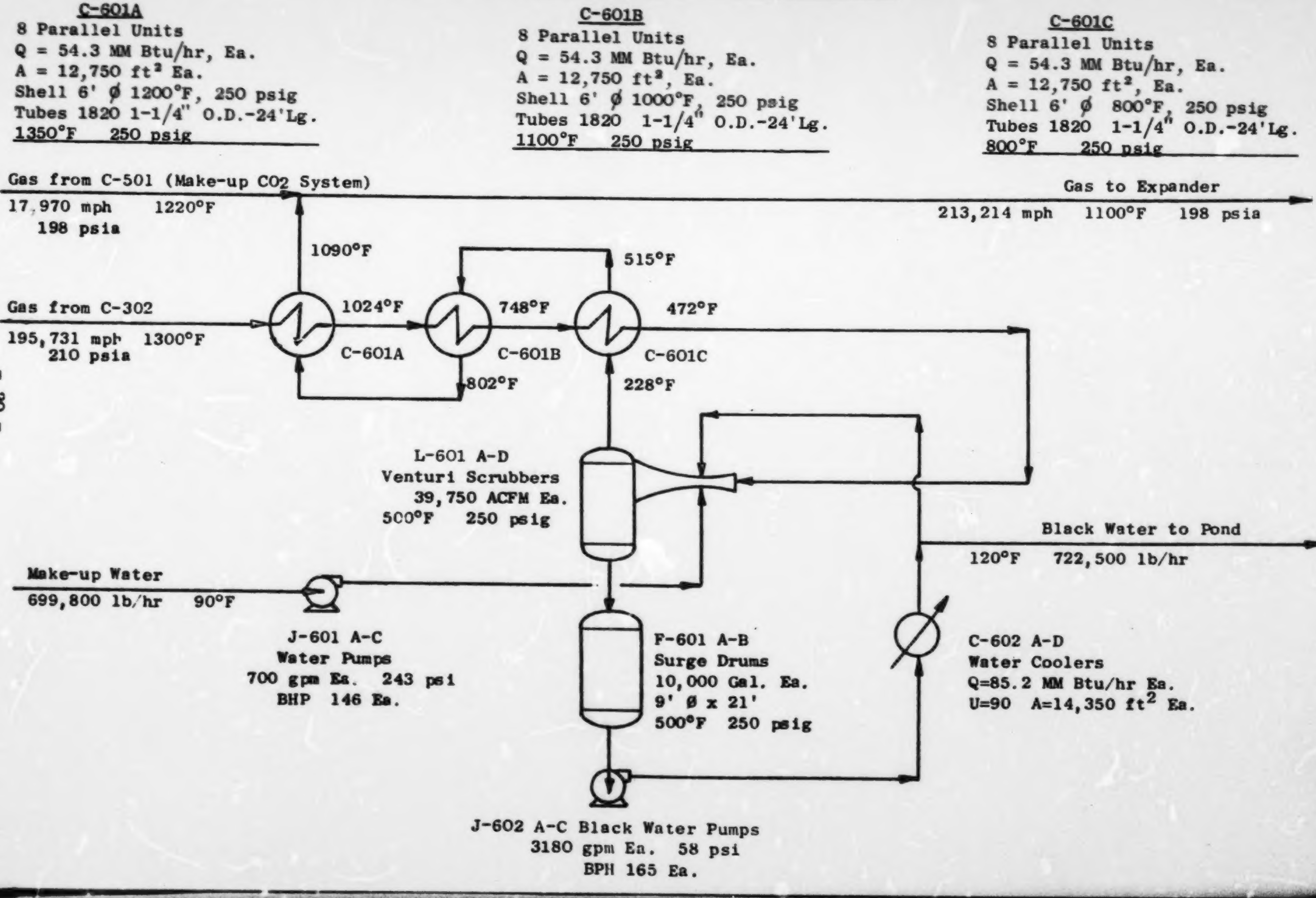
Figure 2

Block Flow Diagram - Overall System


KW
Stack Gas
Make-up CO_2 Removal Section 500
Power Station
Make-up CO_2 Removal Section 500
Desulfurized Producer Gas
Make-up CO_2
Feed Coal
Coal Preparation Section 100
Gasification Section 200
Producer Gas
Sulfur Removal Section 300
Sulfur Recovery Section 400
Ash
Sulfur

Note: Alternative locations of Section 500 shown by dotted lines.

FIGURE 3
Alternative Gas Clean-up System for Particulates
Section 600
Wet Scrubbing with Gas Reheat


C-601A
8 Parallel Units
Q = 54.3 MM Btu/hr, Ea.
A = 12,750 ft² Ea.
Shell 6' Ø 1200°F, 250 psig
Tubes 1820 1-1/4" O.D.-24'Lg.
1350°F 250 psig
C-601B
8 Parallel Units
Q = 54.3 MM Btu/hr, Ea.
A = 12,750 ft², Ea.
Shell 6' Ø 1000°F, 250 psig
Tubes 1820 1-1/4" O.D.-24'Lg.
1100°F 250 psig
C-601C
8 Parallel Units
Q = 54.3 MM Btu/hr, Ea.
A = 12,750 ft², Ea.
Shell 6' Ø 800°F, 250 psig
Tubes 1820 1-1/4" O.D.-24'Lg.
800°F 250 psig
Gas from C-501 (Make-up CO2 System)
17,970 mph 1220°F
198 psia
Gas to Expander
213,214 mph 1100°F 198 psia
1090°F
515°F
Gas from C-302
195,731 mph 1300°F
210 psia
1024°F
748°F
472°F
C-601A
C-601B
C-601C
802°F
228°F
L-601 A-D
Venturi Scrubbers
39,750 ACFM Ea.
500°F 250 psig
Black Water to Pond
120°F 722,500 lb/hr
Make-up Water
699,800 lb/hr 90°F
J-601 A-C
Water Pumps
700 gpm Ea. 243 psi
BHP 146 Ea.
F-601 A-B
Surge Drums
10,000 Gal. Ea.
9' Ø x 21'
500°F 250 psig
C-602 A-D
Water Coolers
Q=85.2 MM Btu/hr Ea.
U=90 A=14,350 ft² Ea.
J-602 A-C Black Water Pumps
3180 gpm Ea. 58 psi
BPH 165 Ea.

Sulfur Removal

A schematic flow diagram of the proposed commercial embodiment of this gas desulfurization process is shown in Figure 4 (Consol Drawing No. AF-3424).

Gasifier product gas (Stream No. 4) flows to the bottom of a fluidized gas desulfurizer (D-301). The gas fluidizes a bed of sized dolomite at a temperature of 1652°F and at 15 atm. absolute pressure. Most (97%) of the H_2S in the gasifier gas reacts with the $CaCO_3$ component of the dolomite as follows:

$$H_2S + MgO \cdot CaCO_3 = MgO \cdot CaS + CO_2 + H_2O.$$

The desulfurized gasifier gas then passes through two stages of cyclones (G-301 and G-302, respectively) to remove substantially all of the fines including attrited acceptor and entrained ash. A portion of the sensible heat content of the desulfurized gas is used to generate and superheat the steam required for gasification of the feed coal in heat exchangers C-302 and C-301, respectively. The desulfurized producer gas at 1300°F and 210 psia (Stream No. 6) is then delivered to the power station. Subsequent use of this gas is dependent on the design of the power station, and is discussed in other sections of this report.

Regenerated acceptor (Stream No. 5) at 1300°F is continuously charged to the top of the gas desulfurizer; sulfided acceptor is continuously withdrawn via a standleg (Stream No. 7). The sulfided acceptor is pneumatically conveyed by a portion of the required recycle gas (Stream No. 9) to a fluidized acceptor regenerator (D-302). Make-up acceptor (Stream No. 8) is introduced into the system by a lockhopper system comprised of L-301, F-301, F-302, and L-302. This small stream is also pneumatically conveyed to D-302 by means of recycle gas. Make-up CO_2 required in D-302 (Stream No. 10) is pressurized by JC-301 and charged to D-302.

The fluidized acceptor regenerator (D-302) is maintained at 1300°F and 15 atm. absolute pressure. The sulfided acceptor is recarbonated at these conditions by the reverse reaction,

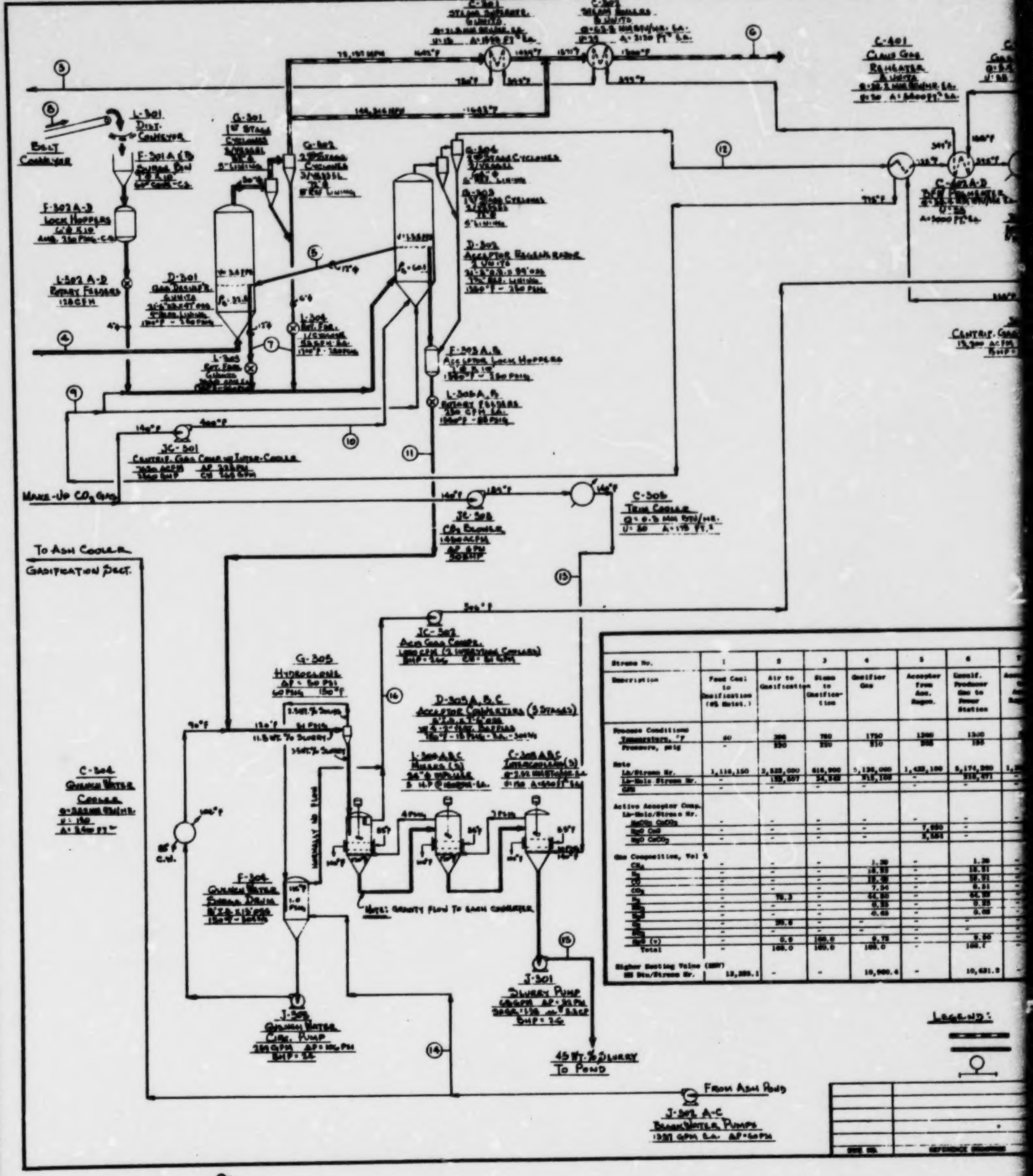
$$MgO \cdot CaS + CO_2 + H_2O = MgO \cdot CaCO_3 + H_2S.$$

The carbonated magnesium component of the make-up acceptor is also calcined at these conditions,

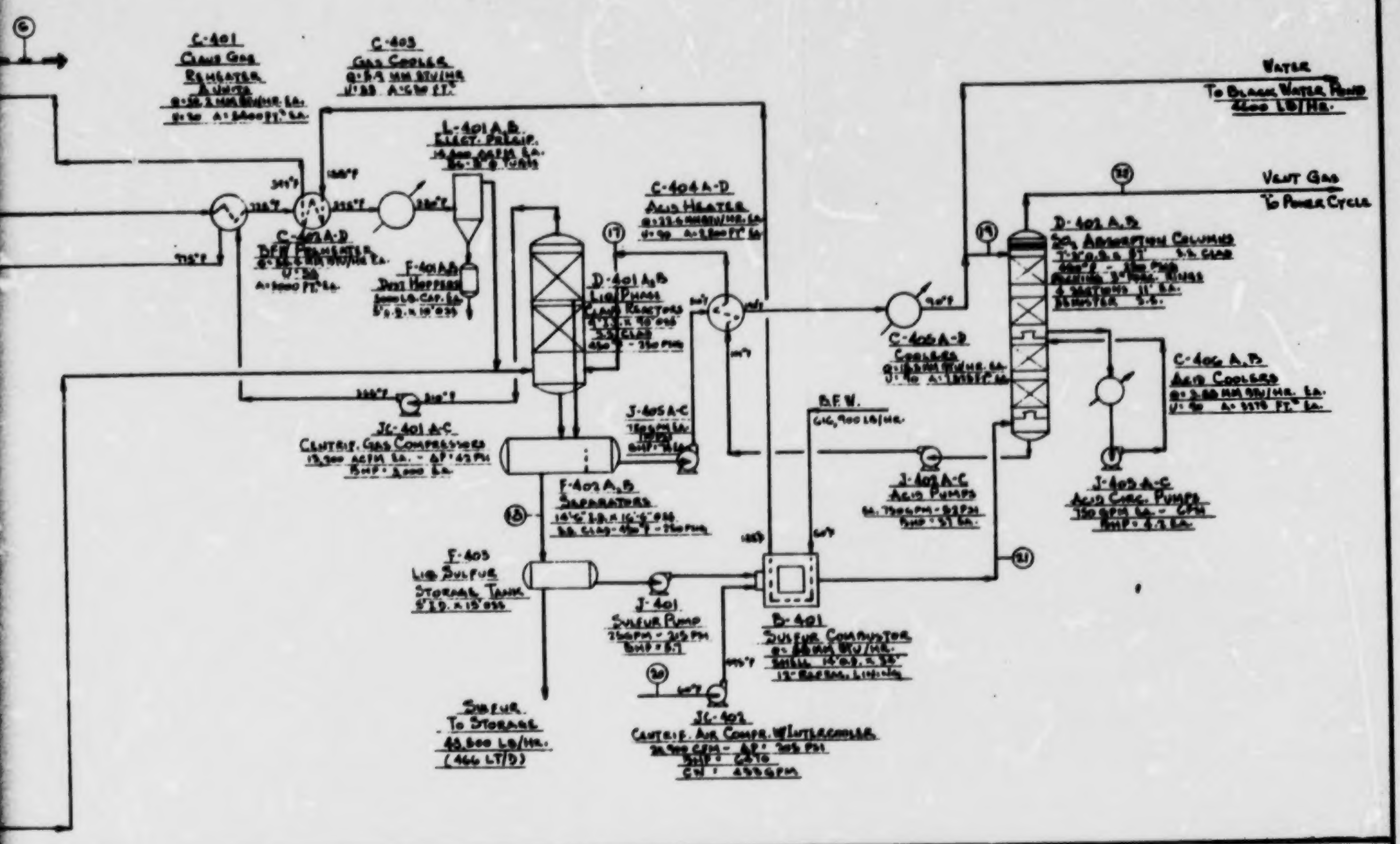
$$MgCO_3 \cdot CaCO_3 = MgO \cdot CaCO_3 + CO_2.$$

The regenerated acceptor is returned to the gas desulfurizer by gravity flow (Stream No. 5). Spent acceptor (1% of the circulating flow) is withdrawn from D-302 via a lockhopper, F-303, and a rotary feeder, L-305 (Stream No. 11). This spent acceptor must be treated before disposal. About 75% of the calcium component of this stream is in the form of CaS. If this were disposed of directly to the station ash pit, H_2S gas would slowly evolve as the CaS was hydrolyzed. To avoid this unacceptable condition, the spent acceptor is directly contacted with CO_2 and water in three stages of stirred reactors, D-303, to convert the CaS to $CaCO_3$. At these conditions, the MgO component of the dolomite would also recarbonate. The overall reaction is,

$$MgO \cdot CaS + 2\ CO_2 + H_2O = MgCO_3 \cdot CaCO_3 + H_2S.$$


C-301
Steam Superheater
C-302
Steam Boilers
79,150 MPH
144,344 MPH
L-301
Dist. Conveyor
Belt Conveyor
F-301 A & B
F-302 A-D
Lock Hoppers
L-302 A-D
Rotary Feeders
128 CFM
G-301
1st Stage Cyclones
G-302
2nd Stage Cyclones
D-301
Gas Desulf'r.
L-303
L-304
G-304
G-303
D-302
Acceptor Regenerator
F-303 A, B
Acceptor Lock Hoppers
L-305 A, B
Rotary Feeders
C-401
Claus Gas Reheater
C-402 A-D
Centrif. Gas
JC-301
Centrif. Gas Comp. w/ Inter-Cooler
Make-Up CO₂ Gas
JC-302
CO₂ Blower
C-306
Trim Cooler
To Ash Cooler
Gasification Sect.
JC-303
Ash Gas Comp.
G-305
Hydroclones
D-303 A, B, C
Acceptor Converters (3 Stages)
L-306 A, B, C
Mixers (3)
C-305 A, B, C
Intercoolers (3)
Note: Gravity Flow To Each Converter
C-304
Quench Water Cooler
F-304
Quench Water Surge Drum
J-302
Quench Water Circ. Pump
J-301
Slurry Pump
45 Wt. % Slurry To Pond
From Ash Pond
J-303 A-C
Black Water Pumps
Legend:
A
3
4
5
6
7
8
9
10
11
12
13
14
15
16

Stream No.	1	2	3	4	5	6
Description	Feed Coal to Gasification (6% Moist.)	Air to Gasification	Steam to Gasification	Gasifier Gas	Acceptor from Acc. Regen.	Desulf. Producer Gas to Power Station
Process Conditions						
Temperature, °F	60	300	750	1750	1900	1300
Pressure, psig	-	330	330	310	300	185
Rate						
Lb/Stream Hr.	1,116,150	3,322,000	616,900	5,136,000	1,422,100	5,174,200
Lb-Mole Stream Hr.	-	115,507	34,243	315,100	-	315,471
GPM	-	-	-	-	-	-
Active Acceptor Comp. Lb-Mole/Stream Hr.						
MgCO₃ CaCO₃	-	-	-	-	-	-
MgO CaO	-	-	-	-	7,950	-
MgO CaCO₃	-	-	-	-	2,584	-
Gas Composition, Vol %						
CH_4	-	-	-	1.20	-	1.20
H_2	-	-	-	14.93	-	15.31
CO	-	-	-	17.40	-	17.11
CO_2	-	-	-	7.34	-	8.31
N_2	-	78.3	-	46.80	-	46.39
[illegible]	-	-	-	0.35	-	0.25
[illegible]	-	-	-	0.66	-	0.08
[illegible]	-	20.8	-	-	-	-
[illegible]	-	-	-	-	-	-
H_2O (v)	-	0.9	100.0	9.72	-	9.50
Total	-	100.0	100.0	100.0	-	100.7
Higher Heating Value (HHV) MM Btu/Stream Hr.	13,285.1	-	-	10,900.4	-	10,631.2


⑥
C-401
Claus Gas Reheater 2 Units
Q=58.2 MM BTU/HR. EA.
U=30 A=8400 FT.² EA.
C-403
Gas Cooler
Q=5.9 MM BTU/HR
U=33 A=630 FT.²
C-402 A-D
DFR Preheater
U=30
A=5000 FT.² EA.
L-401 A,B
Elect. Precip.
14,800 ACFM EA.
F-401 A,B
Dust Hoppers
5' O.D. x 10' O.S.S.
D-401 A,B
Liq. Phase Claus Reactors
SS Clad
450°F - 350 PSIG
J-405 A-C
JC-401 A-C
Centrif. Gas Compressors
13,300 ACFM EA. - ΔP=42 PSI
BHP=2000 EA.
F-402 A,B
Separators
14'6" I.D. x 16'6" O.S.S.
SS Clad - 450°F - 350 PSIG
⑰
⑱
C-404 A-D
Acid Heater
U=90 A=2800 FT.² EA.
C-405 A-D
Coolers
U=90 A=1315 FT.² EA.
B.F.W.
616,900 LB/HR.
F-403
Liq. Sulfur Storage Tank
5' I.D. x 15' O.S.S.
J-401
Sulfur Pump
25 GPM - 215 PSI
BHP=5.7
B-401
Sulfur Combustor
Shell 14' O.D. x 35'
12" Refrac. Lining
⑳
JC-402
Centrif. Air Compr. W/Intercooler
20,900 CFM - ΔP=205 PSI
BHP=6510
CW=455 GPM
Sulfur To Storage
45,600 LB/HR.
(466 LT/D)
Water
To Black Water Pond
4600 LB/HR.
㉒
Vent Gas
To Power Cycle
⑲
D-402 A,B
SO_2 Absorption Columns
S.S. Clad
Packing 3" Porc. Rings
Demister S.S.
C-406 A,B
Acid Coolers
Q=2.80 MM BTU/HR. EA.
U=90 A=3370 FT.² EA.
J-402 A-C
Acid Pumps
BHP=57 EA.
J-403 A-C
Acid Circ. Pumps
350 GPM EA.
BHP=4.3 EA.
㉑
780°F
340°F
715°F
310°F
200°F
90°F

Key Stream Identification-Rates and Process Conditions

	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
al ion s.)	Air to Gasification	Steam to Gasification	Gasifier Gas	Acceptor from Acc. Regen.	Desulf. Producer Gas to Power Station	Acceptor to Acc. Regen.	Make-up Acceptor	Recycle Gas from Liq. Phase Claus Unit	Make-up CO_2 Gas	Acceptor to Stripping Column	Gas To Liq. Phase Claus Unit	Make-up CO_2 Gas	Water from Pond	Slurry to Black Water Pond (45 Wt.% Conc.)	Acid Gas to Liq. Phase Claus Unit	Dilute H_2SO_4 from Absorber	Liquid Sulfur	Water from Liq. Phase Claus Unit	Air to Sulfur Comb.	Gas to SO_2 Absorber	Vent Gas to Power Cycle
	300	780	1730	1300	1200	1652	60	873	400	1300	1300	140	90	120	120	220	310	90	80	400	80
	250	250	310	300	185	235	-	230	290	15	304	10	1	42	1	188	101	190	0	194	180
00	2,585,000	616,900	5,126,000	1,425,100	5,174,200	1,393,200	21,150	1,375,100	12,900	14,290	1,601,250	10,880	26,050	47,000	5,000	775,000	46,600	725,000	98,200	117,230	72,280
	185,607	34,240	913,150	-	316,071	-	-	30,637	1,221	-	30,707	370	-	-	141	42,014	-	-	2,312	2,313	1,610
	-	-	-	-	-	-	-	-	-	-	-	-	55	65	-		-		-	-	-
	-	-	-	-	-	-	105	-	-	78	-	-	-	105	-	-	-	-	-	-	-
	-	-	-	7,980	-	8,365	-	-	-	25	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	3,384	-	1,319	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	1.20	-	1.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	16.22	-	16.51	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	15.42	-	18.51	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	7.54	-	0.31	-	-	64.21	85.3	-	63.56	85.3	-	-	28.6	-	-	-	-	-	-
	79.3	-	44.90	-	44.59	-	-	-	-	-	-	-	-	-	-	-	-	-	79.2	79.2	89.6
	-	-	0.35	-	0.25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	0.08	-	0.08	-	-	0.36	-	-	3.81	-	-	-	54.0	-	-	-	-	-	-
	20.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	20.8	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	20.0	0.2
	0.9	100.0	9.73	-	9.90	-	-	35.21	14.7	-	35.64	14.7	-	-	11.4	-	-	-	0.0	0.8	9.2
	100.0	100.0	100.0	-	100.7	-	-	100.0	100.0	-	100.0	100.0	-	-	100.0	-	-	-	100.0	100.0	100.0
5.1	-	-	10,960.4	-	10,631.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

LEGEND:

Producer Gas Flow

Acceptor Flow

Stream Number

Figure 4

CONSOLIDATION COAL COMPANY
RESEARCH DIVISION
LIBRARY, PENNA.

Process Flow Diagram
Low Sulfur Boiler Fuel
Regenerative Acceptor Case
EPA Contract No. EHSD-71-15

DATE 5-30-73
DWN. W.A.D.
CHK.
APP.
ISSUED FOR CONST.

SCALE	PROJECT NO.	DRAWING NUMBER	REV.
None	553-00	AF-3424	1

NO.	DATE	REVISION	BY	CHK.	APP.
1	8-10-73	General Revisions			

DWG. NO.	REFERENCE DRAWINGS

B

The spent acceptor is conveyed hydraulically by a dilute recirculating slurry stream to a hydroclone, G-305. The underflow slurry (controlled at 35 wt. % solids) flows to the three series converters, D-303A, B and C, respectively. Each converter is agitated by a turbine-type mixer, L-305, and some reaction heat is removed in each stage by cooler, C-305. The spent acceptor, stripped of sulfur and fully carbonated, is pumped to the station ash pit by slurry pump, J-301. The overflow slurry from hydroclone, G-305, is continuously recirculated via surge drum, F-304 and circulating pump, J-303. The sensible heat loss from the spent acceptor is removed by cooler, C-304. Make-up water to this system is supplied by station pond overflow via J-302 (which also supplies the water to cool the gasifier ash and convey it to the station ash pond).

Acid gas resulting from the acceptor stripping operation (Stream No. 16) is compressed to system pressure by JC-302 and flows to the liquid-phase Claus reactor.

Sulfur Recovery

The process gas exiting D-302 (Stream No. 12) is passed through two stages of cyclones (G-303 and G-304, respectively), to remove entrained acceptor. The sensible heat content of this stream is then exchanged with recycle gas in exchanger C-401, and with boiler feed water (required for gasification steam) in C-402. An electrostatic precipitator, L-401, is provided to remove all entrained dust. The gas then flows to the bottom of the liquid-phase Claus reactor, D-401.

The concentration of H_2S in the gas from the acceptor regenerator is limited by the equilibrium restriction at 1300°F and amounts to only about 3.6 volume percent. The liquid-phase Claus reaction developed in this work is uniquely suited to processing this gas. The liquid-phase Claus reactor, D-401, operates at 310°F and about 210 psia. Product gas from the acceptor regenerator (Stream No. 12), gas from the reject acceptor stripping section (Stream No. 16), and dilute, aqueous H_2SO_3 (Stream No. 17) are charged to the bottom of the liquid-phase Claus reactor. Flow is upward through a sparged reactor containing only water, as was demonstrated during the experimental work described in Section XI. Liquid sulfur is produced by the reaction,

$$2\ H_2S + H_2SO_3 = 3\ S + 3\ H_2O.$$

Liquid sulfur and liquid water flow from the reactor to a decanter-type separator, F-402. Unreacted gas (Stream No. 9), saturated with water vapor at 310°F, is compressed by JC-401, reheated in exchanger, C-401 to 975°F and returned to the acceptor regenerator reactor. The sensible heat content of the liquid water from F-402 (Stream No. 19), is exchanged with the feed acid (Stream No. 17) in C-404, further cooled to 90°F in C-405 and charged to the SO_2 absorption tower, D-402.

Approximately one-third of the sulfur from F-402 is burned with stoichiometric air (Stream No. 20) in pressurized combustor, B-401, to produce SO_2. Excess heat is removed to boiler feed water via cooling tubes in the walls. The exit gas from the sulfur combustor (Stream No. 21) flows to the base of the SO_2 absorption tower, D-402. Water (Stream No. 19) flowing down through the packed tower absorbs the SO_2 in the gas by,

$$SO_2 + H_2O = H_2SO_3 \text{ aqueous}$$

Most of the exothermic heat of reaction is removed by side stream cooler, C-406. The vent gas from the absorption tower (Stream No. 22) is at 90°F and 205 psia. It probably would contain some residual SO_2 (assumed in this case as 0.3 volume percent). The most practical means of disposing of this gas is to bleed it to an intermediate stage of the expansion turbine required for the desulfurized producer gas in the power station. This would decrease the sulfur removal efficiency of this process from 97.0% to 96.5%, but would increase the power output of the station slightly, and would eliminate an entire stack gas scrubbing installation following the SO_2 absorption step.

Wet Scrubbing - Gas Reheat

For the case where the product gas must be wet scrubbed (for particulate and alkali removal), then reheated for use in an expanding turbine, the additional equipment in Section 600 (Figure 3) is required.

That portion of the process gas exiting from the gas desulfurization system that is not charged to the make-up CO_2 system (Section 500) is available at 1300°F and 210 psia. The gas is cooled to 472°F by heat exchange with the scrubbed gas in three series steps (C-601A, B, and C, successively). The cooled gas then flows to four parallel Venturi scrubbers (L-601) where it is scrubbed by circulating water at the gas dewpoint of 228°F. The clean gas exiting the scrubbers is then reheated to 1090°F by the aforementioned exchangers (C-601). This cleaned, reheated gas, combined with the product gas diverted to the make-up CO_2 system, comprises the total product gas flow to the power station. The combined gas is at a tempterature of 1100°F and at a pressure of 198 psia.

The circulating water flow to the Venturi scrubbers flows via surge drums F-601 and black water pumps, J-602. The excess sensible heat in the gas is removed via coolers, C-602. Make-up water enters the system via water pumps, J-601. The make-up water rate is based on an assumed solids loading in the process gas of 5 grains/cubic foot, and a solids content in the circulating water of 2 wt. %. Net solids removed from the gas flow as a 2 wt. % slurry to the station pond.

E. Design Basis

Gasification

Although the detailed design and evaluation of the gasification system is not covered in this study, it is of interest to at least relate the composition of the raw gasifier gas to the input feed streams to the gasification section.

1. Feed Coal

This study is based on the use of a high-sulfur content, highly-caking Pittsburgh Seam coal. The analyses of a typical coal (Ireland Mine) of this seam is shown below:

Feed Coal Analysis

Moisture, as received	6.0 wt %
Ultimate Analysis, MF basis	
Hydrogen	4.8 wt %
Carbon	69.8 wt %
Nitrogen	1.2 wt %
Oxygen	7.6 wt %
Sulfur	4.3 wt %
Ash	12.3 wt %
Higher Heating Value, MF basis	12,700 Btu/lb

2. Other Design Constraints

The total sensible heat content of the gasifier steam is supplied by heat exchange within the sulfur removal and sulfur recovery sections. Additional design constraints for the fluidized bed gasifier and carbon burn-up cell are:

System Pressure	15 atm.
Gasifier Temperature	1750°F
Gasification Rate	0.00883 lb C/min-lb C in bed
Steam Conversion in Gasifier	52.9%
Burn-up Cell Temperature	1800°F
Percent Total Carbon to Burn-up Cell	13.4%

Gas Desulfurizer

The sulfur in the producer gas (as H_2S) is removed in the gas desulfurizer by reaction with $CaCO_3$ as follows:

$$MgO\cdot CaCO_3 + H_2S = MgO\cdot CaS + CO_2 + H_2O$$

The commercial design basis for this study is adopted from the actual experimental data which are reviewed in a later section of this report. Pertinent design values are:

Desulfurizer Temperature	1652°F
Desulfurizer Pressure	15 atm.
Avg. Acceptor Size, Dp arithmetic mean	0.065 inch
Acceptor Density, ρ_s	130 lb/CF
Mol % Ca as CaS - Inlet Acceptor	75.4%
Mol % Ca as CaS - Outlet Acceptor	88.4%
$\left(\frac{\text{Mols CaS}}{\text{Mols Ca}}\right)$ Out - $\left(\frac{\text{Mols CaS}}{\text{Mols Ca}}\right)$ In	0.13⁽¹⁾
Avg. Acceptor Residence Time	30 min.
Outlet Fluidizing Velocity	3.4 ft/sec
Approach to Equilibrium $(H_2O)(CO_2)/H_2S$	100%
Removal of H_2S from Producer Gas	97%
CO_2 Driving Force	0.147 atm.

(1) Excluding make-up acceptor.

(2) p_{CO_2} - equilibrium p_{CO_2} for the reaction, $CaCO_3 = CaO + CO_2$.

Acceptor-Regenerator

The highly-sulfided acceptor from the gas desulfurizer is regenerated (converted to $CaCO_3$) at a low temperature by the reverse reaction,

$$MgO \cdot CaS + CO_2 + H_2O = MgO \cdot CaCO_3 + H_2S.$$

Again, the commercial design basis for this study is adopted directly from the actual experimental data. Note that the small yields of COS and S_2 actually detected in the experimental program have been ignored in this study. Presumably these compounds are formed from the reactions:

$$H_2S + CO_2 = COS + H_2O$$

$$2\ H_2S = S_2 + 2\ H_2$$

It is assumed that, for long-term operation, an equilibrium concentration of COS and H_2 would be established in the recycle gas and completely inhibit further reaction.

The acceptor make-up requirement was arrived at by extrapolation of data from the continuous unit. The sulfur absorption was assumed to be 13% of the total calcium for 13 cycles, and then decline exponentially to zero at infinite cycles. The rate of decline was assumed to be sufficiently small to permit a 1% make-up rate.

The required make-up acceptor (as $MgCO_3 \cdot CaCO_3$) is charged to the acceptor-regenerator. The $MgCO_3$ component of the dolomite is completely calcined at these conditions as follows:

$$MgCO_3 \cdot CaCO_3 = MgO \cdot CaCO_3 + CO_2$$

Other pertinent design values for the commercial acceptor-regenerator are:

Regenerator Temperature	1300°F
Regenerator Pressure	15 atm.
Avg. Acceptor Size, Dp arithmetic mean	0.065 inch
Acceptor Density, ρ_s	132 lb/CF
Mol % Ca as CaS - Inlet Acceptor(1)	88.4%
Mol % Ca as CaS - Outlet Acceptor(1)	75.4%
$\left(\frac{\text{Mols CaS}}{\text{Mols Ca}}\right)$ In - $\left(\frac{\text{Mols CaS}}{\text{Mols Ca}}\right)$ Out	0.13(1)
Avg. Acceptor Residence Time	60 min.
Outlet Fluidizing Velocity	1.55 ft/sec
Approach to Equilibrium, $(H_2O)(CO_2)/H_2S$	87%

(1) Excluding make-up acceptor.

Acceptor Converters

In this process the spent acceptor to be rejected from the system must be converted from $MgO \cdot CaS$ to $MgCO_3 \cdot CaCO_3$ before disposal. In the unconverted state, the acceptor would slowly release H_2S to the atmosphere.

The conversion is by the chemical reaction,

$$MgO \cdot CaS + 2\ CO_2 + H_2O = MgCO_3 \cdot CaCO_3 + H_2S.$$

Data for the design of the acceptor converters was obtained from the Bureau of Mines staff at Salt Lake City. These data are not yet published.

Pertinent design values are:

Conversion Temperature	120°F
Conversion Pressure	Atmospheric
Wt. % Acceptor in Slurry	45
No. Stages Required	3
Utilization of CO_2	80%
Conversion of CaS to $CaCO_3$	Approaching 100%

Liquid-Phase Claus

The offgas from the acceptor regenerator is passed cocurrently through a reactor with a stream of aqueous H_2SO_3 where the following reaction occurs,

$$2\ H_2S + H_2SO_3 = 3\ S + 3\ H_2O.$$

The design basis is taken directly from the experimental results from Runs C-9, C-10, and C-11 as follows:

Reactor Temperature	320°F
Reactor Pressure	14 atm.
Volumetric Space Rate	1340 hr^{-1}
Outlet Gas Velocity	0.25 ft/sec.
Avg. Vapor Residence Time	27 sec.
Conversion H_2S to S	90%

SO_2 Absorption Column

The dilute H_2SO_3 required in the liquid-phase Claus reactor is produced by absorption of SO_2 in water in a standard countercurrent flow packed tower. The design is based on published data for the system.(9,10) Key design parameters are:

Absorber Temperature	90-110°F
Absorber Pressure	14 atm.
Liquid Rate	10,000 $lb/hr\text{-}ft^2$
Packing	3" porcelain rings
No. Stages	4
Outlet Vapor Velocity	0.27 ft/sec
Percent Flooding Velocity	50%

F. Material and Heat Balances

Basic to the process design and economic evaluation of this process on a commercial scale was the completion of mass and heat balances for each important processing step. The capacity of the plant in this study (with respect to the total heating value of the desulfurized producer gas), is the same as in the initial feasibility study.(1) This plant would supply a modern conventional gas-fired power station of approximately 1400 MW rating.

The computer program developed by Consol for the integrated system of coal preoxidation, gasification, carbon burn-up cell and producer gas desulfurization has been described earlier in this section.

With these calculations as a starting point, the following mass and heat balances were evolved for the commercial process design:

Table 4 - Gas Desulfurizer
Table 5 - Acceptor Regenerator
Table 6 - Spent Acceptor Stripping
Table 7 - Liquid-Phase Claus Reactor
Table 8 - Sulfur Combustor
Table 9 - SO_2 Absorption Column
Table 10 - Over-all Mass and Heat Balance

These balances define the regenerable acceptor case. As is covered later, it was not necessary to define in this detail the once-through acceptor system.

G. Economic Evaluation

Introduction and Scope

The process under development in this work produces a desulfurized producer gas, under pressure, as a desirable fuel gas for power generation. In the first Annual Report on this project,(1) it was clearly demonstrated that the most economic application of the process was in combination with a pressurized combined cycle power station. However, these advanced power generation techniques are only now under development. This study is restricted to delivery of the desulfurized gas to a conventional gas-burning station at a pressure of 10 psig.

The pressurized producer gas must be expanded from system pressure (about 200 psig) to 10 psig. This is best accomplished in an expanding turbine-generator set. The power output from this unit exceeds the power requirement to compress the air for the coal gasification step. The excess power so recovered is a net credit to the process. However, it is beyond the scope of this contract to define the actual dollar value of the power credit.

There remains a technical question as to the required quality of gas (with respect to content and size of particulate matter and alkali) that may be charged to an expander. It is obvious that the maximum power will be recovered from the expanding turbine if the pressurized producer gas can be adequately "cleaned" by high pressure drop cyclones alone. Conversely, the gas may be water scrubbed (in conventional Venturi scrubbers) then reheated by indirect heat exchange with hot gas to the scrubbers. This variation assures that the expansion turbine is protected from particle erosion and/or alkali deposition. There is, of course, a reduction in the power recovery possible since the gas can only be reheated (economically) to about 1100°F, and there is a pressure drop through the scrubbing and reheating system (estimated in this study as 12 psi).

A review of the "state of the art" on the use of high-pressure drop cyclones to remove particulate matter from a gas feed to a turbine is included in a recent Westinghouse report to EPA.(11)

In this study two cases are presented to cover the range of this technical uncertainty:

Case I - "Hot clean-up" by cyclones only.
Case II - Wet scrubbing with gas reheat.

Table 4

Mass and Heat Balance
Gas Desulfurizer

Basis: 1 hour   Datum: 60°F, H_2O (l)

	Lb	M.W.	Mols	Mol %	Elemental Balance, Lb							Temp. °F	Δh	ΔH MM Btu	HHV	
					H	C	N	O	S	Ash	MgO Ca				Unit Btu/lb	Total MM Btu
Input																
④ **Gasifier Gas**																
CH_4	47,950	16.04	2,990	1.39	12,050	35,900	x	x	x	x	x	1750	24,125 Btu/mol	72.1	23,878	1,145.2
H_2	70,350	2.016	34,899	16.23	70,350	x	x	x	x	x	x	1750	11,643 Btu/mol	406.3	61,100	4,298.8
CO	1,170,250	28.01	41,779	19.42	x	501,750	x	668,500	x	x	x	1750	12,924 Btu/mol	540.0	4,347	5,087.0
CO_2	713,400	44.01	16,210	7.54	x	194,700	x	518,700	x	x	x	1750	19,925 Btu/mol	323.0	x	x
N_2	2,700,100	28.02	96,364	44.80	x-	x	2,700,100	x	x	x	x	1750	12,515 Btu/mol	1,206.0	x	x
NH_3	9,150	17.03	539	0.25	1,600	x	7,550	x	x	x	x	1750	24,126 Btu/mol	13.0	9,680	88.9
H_2S	47,950	34.08	1,407	0.65	2,850	x	x	x	45,100	x	x	1750	16,812 Btu/mol	23.7	7,100	340.8
H_2O (v)	376,850	18.016	20,917	9.72	42,200	x	x	334,650	x	x	x	1750	34,492 Btu/mol	721.5	x	x
Sub-Total	5,136,000	-	215,106	100.0	129,050	732,350	2,707,650	1,521,850	45,100	x	x			3,305.6		10,960.4
⑤ **Acceptor from Acc. Regen.**																
MgO CaS	890,700	112.46	7,920	75.4	x	x	x	x	253,900	x	636,800	1300	28,569 Btu/mol	226.3	-	-
MgO $CaCO_3$	362,850	140.41	2,584	24.6	x	31,050	x	124,050	x	x	207,750	1300	45,746 Btu/mol	118.2	-	-
Inerts	178,550	-	-	-	x	-	x	x	x	178,550	x	1300	300.65 Btu/lb	53.7	-	-
Sub-Total	1,432,100	-	10,504	100.0	x	31,050	x	124,050	253,900	178,550	844,550			398.2		-
Totals	6,568,100	-	-	-	129,050	763,400	2,707,650	1,645,900	299,000	178,550	844,550			3,703.8		
Output																
⑥ **Producer Gas**																
CH_4	47,950	16.04	2,990	1.38	12,050	35,900	x	x	x	x	x	1652	22,290 Btu/mol	66.7	23,878	1,145.2
H_2	72,100	2.016	35,750	16.51	72,100	x	x	x	x	x	x	1652	10,969 Btu/mol	392.1	61,100	4,403.8
CO	1,146,400	28.01	40,928	18.91	x	491,550	x	654,850	x	x	x	1652	12,109 Btu/mol	495.6	4,347	4,983.4
CO_2	810,950	44.01	18,427	8.51	x	221,300	x	589,650	x	x	x	1652	18,611 Btu/mol	342.9	x	x
N_2	2,700,100	28.02	96,364	44.52	x	x	2,700,100	x	x	x	x	1652	11,707 Btu/mol	1,128.2	x	x
NH_3	9,150	17.03	539	0.25	1,600	x	7,550	x	x	x	x	1652	22,290 Btu/mol	12.0	9,680	88.9
H_2S	1,450	34.08	43	0.02	100	x	x	x	1,350	x	x	1652	16,683 Btu/mol	0.7	7,100	10.1
H_2O (v)	386,100	18.016	21,431	9.90	43,200	x	x	342,900	x	x	x	1652	33,476 Btu/mol	717.4	x	x
Sub-Total	5,174,200	-	216,471	100.0	129,050	748,750	2,707,650	1,587,400	1,350	x	x			3,155.6		10,631.2
⑦ **Acceptor to Acc. Regen.**																
MgO CaS	1,044,200	112.46	9,285	88.4	x	x	x	x	297,650	x	746,550	1652	37,541 Btu/mol	348.6	-	-
MgO $CaCO_3$	171,150	140.41	1,219	11.6	x	14,650	x	58,500	x	x	98,000	1652	61,274 Btu/mol	74.7	-	-
Inerts	178,550	-	-	-	x	x	x	x	x	178,550	x	1652	398.3 Btu/lb	71.1	-	-
Sub-Total	1,393,900	-	10,504	100.0	x	14,650	x	58,500	297,650	178,550	844,550			494.4		-
Heat of Reaction																
MgO $CaCO_3$ + H_2S = MgO CaS + CO_2 + H_2O (1,365 mols x 30,830 Btu/mol)														42.1		
CO + H_2O = CO_2 + H_2 (851 mols x 1,430 Btu/mol)														1.2		
Heat Loss														10.5		
Totals	6,568,100	-	-	-	129,050	763,400	2,707,650	1,645,900	299,000	178,550	844,550			3,703.8		

Note: Circled numbers refer to Stream Number on Consol Dwg. AF-3424. Temperature/Pressure may differ depending on location of identifying flag.

Table 5

Mass and Heat Balance
Acceptor Regenerator

Basis: 1 hour Datum: 60°F H_2O (l)

	Lb	Mols	Mol %	Temp. °F	ΔH	ΔH MM Btu
Input						
⑦ **Acceptor from Gas Desulfurizer**						
MgO CaS	1,044,200	9,285	88.4	1652	37,541 Btu/mol	348.6
MgO $CaCO_3$	171,180	1,219	11.6	1652	61,274 Btu/mol	74.7
Inerts	178,550	-	-	1652	398.3 Btu/lb	71.1
Sub-Total	1,393,900	10,504	100.0			494.4
⑧ **Make-up Acceptor**						
$MgCO_3$ $CaCO_3$	19,350	105	-	60	-	x
Inerts	1,800	-	-	60	-	x
Sub-Total	21,150	105	-			x
⑨ **Gas from Liquid-Phase Claus**						
CO_2	1,121,800	25,489.5	64.31	975	9,861 Btu/mol	251.4
H_2S	5,160	151.5	0.38	975	8,323 Btu/mol	1.3
H_2O (v)	252,150	13,996	35.31	975	26,840 Btu/mol	375.6
Sub-Total	1,379,100	39,637	100.0			628.3
⑩ **Make-up CO_2 Gas**						
CO_2	49,950	1,135	85.3	400	3,314 Btu/mol	3.7
H_2O (v)	3,550	196	14.7	400	21,738 Btu/mol	4.3
Sub-Total	53,500	1,331	100.0			8.0
Heat of Reaction						
MgO CaS + CO_2 + H_2O = MgO $CaCO_3$ + H_2S (1286 mols x 30,830 Btu/mol)						39.6
Totals	2,847,650					1,170.3
Output						
③ **Acceptor to Gas Desulfurizer**						
MgO CaS	890,700	7,920	75.4	1300	28,569 Btu/mol	226.3
MgO $CaCO_3$	362,850	2,584	24.6	1300	45,746 Btu/mol	118.2
Inerts	178,550	-	-	1300	300.65 Btu/lb	53.7
Sub-Total	1,432,100	10,504	100.0			398.2
⑪ **Acceptor to Stripping Column**						
MgO CaS	8,900	79	75.4	1300	28,569 Btu/mol	2.3
MgO $CaCO_3$	3,650	26	24.6	1300	45,746 Btu/mol	1.2
Inerts	1,800	-	-	1300	300.65 Btu/lb	0.5
Sub-Total	14,350	105	100.0			4.0
⑫ **Gas to Liquid-Phase Claus**						
CO_2	1,119,750	25,443.6	63.98	1300	13,955 Btu/mol	355.0
H_2S	49,000	1,437.8	3.61	1300	11,738 Btu/mol	16.9
H_2O (v)	232,500	12,906	32.44	1300	29,933 Btu/mol	386.3
Sub-Total	1,401,250	39,787	100.0			758.2
Heat of Reaction						
$MgCO_3$ $CaCO_3$ = MgO $CaCO_3$ + CO_2 (105 mols x 42,850 Btu/mol)						4.5
Heat Loss						5.4
Totals	2,847,700	-				1,170.3

Note: Circled numbers refer to Stream Number on Consol Dwg. AF-3424. Temperature/Pressure may differ depending on location of identifying flag.

Table 6

Mass and Heat Balance
Acceptor Stripping Column

Basis: 1 hour Datum: 60°F, H_2O (1)

	Lb	Mols	Temp. °F	ΔH or Cp	ΔH MM Btu
Input					
⑪ Acceptor from Acc. Regen.					
MgO CaS	8,900	79	1300	28,569 Btu/mol	2.26
MgO $CaCO_3$	3,650	26	1300	45,746 Btu/mol	1.19
Inerts	1,800	-	1300	300.65 Btu/lb	0.54
Sub-Total	14,350	105			3.99
⑬ Make-up CO_2 Gas					
CO_2	10,150	230	140	736 Btu/mol	0.17
H_2O (v)	700	40	140	19,708 Btu/mol	0.79
Sub-Total	10,850	270			0.96
⑭ Water (1)	26,850	-	90	29.93 Btu/lb	0.80
Heat of Reaction					
MgO CaS + CO_2 + H_2O = MgO $CaCO_3$ + H_2S (79 mols x 30,830 Btu/mol)					2.44
MgO $CaCO_3$ + CO_2 = $MgCO_3$ $CaCO_3$ (105 mols x 42,850 Btu/mol)					4.50
Totals	52,050				12.69
Output					
⑮ Reject Acceptor to Pond					
$MgCO_3$ $CaCO_3$	19,350	105	120	40.3 Btu/mol-°F	0.25
Inerts	1,800	-	120	0.21 Btu/lb-°F	0.02
Water (1)	25,850	-	120	59.86 Btu/lb	1.55
Sub-Total	47,000	-			1.82
⑯ Acid Gas to Liquid Phase Claus					
CO_2	2,050	46	120	542 Btu/mol	0.02
H_2S	2,700	79	120	491 Btu/mol	0.04
H_2O (v)	300	16	120	1085.6 Btu/lb	0.31
Sub-Total	5,050	141			0.37
Heat Rejected to Cooling Water					10.50
Totals	52,050	-			12.69

Note: Circled numbers refer to Stream Number on Consol Dwg. AF-3424. Temperature/Pressure may differ depending on location of identifying flag.

Table 7
Mass and Heat Balance
Liquid-Phase Claus Reactor

Basis: 1 hour - Datum: 60°F, H_2O (1)

	Lb	Mols	Mol %	Temp. °F	ΔH or Cp	ΔH MM Btu
Input						
⑫ **Gas from Acceptor Regenerator**						
CO_2	1,119,750	25,443.5	63.95	380	3092 Btu/mol	78.7
H_2S	49,000	1,437.5	3.61	380	2695 Btu/mol	3.9
H_2O (v)	232,500	12,906	32.44	380	21,600 Btu/mol	278.6
Sub-Total	1,401,250	39,787	100.0			361.2
⑯ **Gas from Acceptor Stripping Column**						
CO_2	2,050	46	32.6	305	2340 Btu/mol	0.1
H_2S	2,700	79	56.0	305	2049 Btu/mol	0.2
H_2O (v)	300	16	11.4	305	20,756 Btu/mol	0.3
Sub-Total	5,050	141	100.0			0.6
⑰ **Liquid from SO_2 Absorber**						
H_2SO_3	56,000	682.5	1.68	220	1.0 Btu/lb °F	122.3
H_2O (1)	720,650	40,001.5	98.32	220		
Sub-Total	776,650	40,684	100.0			122.3
Heat of Reaction						
$2\ H_2S + H_2SO_3 = 3S + 3\ H_2O$ (1365 mols H_2S x 42,980 Btu/mol)						58.7
Totals	2,182,950	-				542.8
Output						
⑨ **Gas to Acceptor Regenerator**						
CO_2	1,121,800	25,489.5	64.31	310	2391 Btu/mol	60.9
H_2S	5,150	151.5	0.38	310	2092 Btu/mol	0.3
H_2O (v)	252,150	13,996	35.31	310	20,797 Btu/mol	291.1
Sub-Total	1,379,100	39,637	100.0			352.3
⑱ **Sulfur** (1)	65,600	2,047.5	-	310	0.2 Btu/lb °F	3.3
Water (1)	738,200	-	-	310	251.86 Btu/lb	185.9
Heat Loss						1.3
Totals	2,182,900	-				542.8

Note: Circled numbers refer to Stream Number on Consol Dwg. AF-3424. Temperature/Pressure may differ depending on location of identifying flag.

Table 8

Mass and Heat Balance
Sulfur Combustor

Basis: 1 hour   **Datum:** 60°F H_2O (l)

	Lb.	Mols	Temp. °F	ΔH	ΔH MM Btu
Input					
Sulfur(s)	22,100	689.5	60	-	x
⑳ Air					
O_2	22,050	689.5	495	3.044 Btu/mol	9.99
N_2	72,650	2,593.5	495		
H_2O (v)	500	29	495	22,565 Btu/mol	0.66
Sub-Total	95,200	3,312			10.65
Heat Required to Melt S and Preheat to 280°F					1.39
Heat Release by Combustion of Sulfur (689.5 mols x 127,690 Btu/mol)					88.04
Totals	117,300	-			100.08
Output					
㉑ Gas to Absorption Tower					
SO_2	44,150	689.5	400	3487 Btu/mol	2.40
N_2	72,650	2,593.5	400	2258 Btu/mol	5.86
H_2O (v)	500	29	400	1213.6 Btu/lb	0.61
Sub-Total	117,300	3,312			8.87
Heat Transfer to B.F.W. Preheater					80.13
Heat Loss					11.08
Totals	117,300				100.08

Note: Circled numbers refer to Stream Number on Consol Dwg. AF-3424. Temperature/Pressure may differ depending on location of identifying flag.

Table 9

Mass and Heat Balance
SO_2 Absorption Tower

Basis: 1 hour   Datum: 60°F H_2O (1)

	Lb	Mols	Temp. °F	ΔH or Cp	ΔH MM Btu
Input					
㉑ **Gas from Sulfur Combustor**					
SO_2	44,150	689.5	400	3487 Btu/mol	2.40
N_2	72,650	2,593.5	400	2258 "	5.86
H_2O (v)	500	29	400	1213.6 Btu/lb	0.61
Sub-Total	117,300	3,312			8.87
⑲ **Water** (1)	732,600	-	90	29.93 Btu/lb	21.93
Heat of Reaction					
$SO_2 + H_2O = H_2SO_3$ (aq.)					
(682.5 mols x 13,720 Btu/mol)					9.36
Totals	849,900	-			40.16
Output					
㉒ **Vent Gas**					
SO_2	450	7	90	285 Btu/mol	x
N_2	72,650	2,593.5	90	194 "	0.50
H_2O (v)	150	9	90	1072.8 Btu/lb	0.16
Sub-Total	73,250	2,609.5			0.66
⑰ **Liquid**					
H_2SO_3	56,000	682.5	101		
H_2O (1)	720,650	40,001.5	101		
Sub-Total	776,650	40,684		1.0 Btu/lb-°F	31.84
Heat Rejected to Cooling Water					7.66
Totals	849,900	-			40.16

Note: Circled numbers refer to Stream Number on Consol Dwg. AF-3424. Temperature/Pressure may differ depending on location of identifying flag.

Table 10

Over-all Mass and Heat Balance

Basis: 1 hour   Datum: 60°F, H_2O (ℓ)

	Lb	M.W	Mols	Mol%	Elemental Balance, Lb							Temp °F	ΔH or Cp	ΔH MM Btu	Higher Heating Value	
					H	C	N	O	S	Ash	$MgCO_3$				Btu/lb	MM Btu
Input																
④ **Gasifier Gas**																
CH_4	47,950	16.04	2,990	1.39	12,050	35,900	x	x	x	x	x	1750	24,126 Btu/mol	72.1	23,878	1,143.3
H_2	70,350	2.016	34,899	16.23	70,350	x	x	x	x	x	x	1750	11,643 Btu/mol	406.3	61,100	4,298.8
CO	1,170,250	28.01	41,779	19.43	x	501,750	x	668,500	x	x	x	1750	12,924 Btu/mol	540.0	4,347	5,087.0
CO_2	713,400	44.01	16,210	7.54	x	194,700	x	518,700	x	x	x	1750	19,828 Btu/mol	323.0	x	x
N_2	2,700,100	28.02	96,364	44.80	x	x	2,700,100	x	x	x	x	1750	12,515 Btu/mol	1,206.0	x	x
NH_3	9,150	17.03	539	0.25	1,600	x	7,550	x	x	x	x	1750	24,126 Btu/mol	13.0	9,680	88.9
H_2S	47,950	34.08	1,407	0.65	2,850	x	x	x	45,100	x	x	1750	16,013 Btu/mol	23.7	7,100	340.5
H_2O (v)	376,850	18.016	20,917	9.72	42,200	x	x	334,650	x	x	x	1750	34,493 Btu/mol	721.5	x	x
Sub-Total	5,136,000		215,106	100.0	129,050	732,350	2,707,650	1,521,850	45,100	x	x			3,305.6		10,960.4
⑧ **Make-up Acceptor**																
K_2CO_3 $CaCO_3$	19,350	184.42	105	-	x	2,500	x	8,400	x	x	8,450	60	-	x	-	-
Inerts	1,800	-	-	-	x	x	x	x	x	1,800	x	60	-	x	-	-
Sub-Total	21,150		-	-	x	2,500	x	8,400	x	1,800	8,450			x		
⑳ **Air to Sulfur Combustor**																
O_2	22,050	32.00	689.5	20.8	x	x	x	22,050	x	x	x	60	-	x	x	x
N_2	72,650	28.02	2,593.5	78.3	x	x	72,650	x	x	x	x	60	-	x	x	x
H_2O (v)	500	18.016	29.	0.9	50	x	x	450	x	x	x	60	19,093 Btu/mol	0.5	x	x
Sub-Total	95,200		3,312	100.0	50	x	72,650	22,500	x	x	x			0.5		x
Make-up CO_2 Gas																
CO_2	60,100	44.01	1,365	85.3	x	16,400	x	43,700	x	x	x	140	736 Btu/mol	1.0	x	x
H_2O (v)	4,250	18.016	236	14.7	500	x	x	3,750	x	x	x	140	19,706 Btu/mol	4.6	x	x
Sub-Total	64,350		1,601	100.0	500	16,400	x	47,450	x	x	x			5.6		x
Heat of Compression														31.3		
Heat of Reaction																
$H_2S + 1/2\ O_2 = S + H_2O$ (1.358 mols H_2S x 113,920 Btu/mol)														154.7		
$H_2S + 3/2\ O_2 = SO_2 + H_2O$ (7 mols H_2S x 242,080 Btu/mol)														1.7		
Totals	5,316,700				129,600	751,250	2,780,300	1,600,200	45,100	1,800	8,450			3,499.4		
Output																
⑥ **Producer Gas**																
CH_4	47,950	16.04	2,990	1.38	12,050	35,900	x	x	x	x	x	1300	16,014 Btu/mol	47.9	23,878	1,143.2
H_2	72,100	2.016	35,750	16.51	72,100	x	x	x	x	x	x	1300	8,533 Btu/mol	305.1	61,100	4,403.6
CO	1,146,400	28.01	40,928	18.91	x	491,550	x	654,850	x	x	x	1300	9,228 Btu/mol	377.7	4,347	4,983.4
CO_2	810,950	44.01	18,427	8.51	x	221,300	x	589,650	x	x	x	1300	13,955 Btu/mol	257.1	x	x
N_2	2,700,100	28.02	96,364	44.52	x	x	2,700,100	x	x	x	x	1300	8,870 Btu/mol	854.8	x	x
NH_3	9,150	17.03	539	0.25	1,600	x	7,550	x	x	x	x	1300	16,014 Btu/mol	8.6	9,680	88.6
H_2S	1,450	34.08	42	0.02	100	x	x	x	1,350	x	x	1300	11,735 Btu/mol	0.5	7,100	10.1
H_2O (v)	386,100	18.016	21,431	9.90	43,200	x	x	342,900	x	x	x	1300	29,932 Btu/mol	641.3	x	x
Sub-Total	5,174,200		216,471	100.0	129,050	748,750	2,707,650	1,587,400	1,350	x	x			3,493.2		10,631.2
⑮ **Reject Acceptor**																
K_2CO_3 $CaCO_3$	19,350	184.42	105	-	x	2,500	x	8,400	x	x	8,450	120	40.3 Btu/mol °F	0.3	-	-
Inerts	1,800	-	-	-	x	x	x	x	x	1,800	x	120	0.21 Btu/lb °F	x	-	-
Sub-Total	21,150		-	-	x	2,500	x	8,400	x	1,800	8,450			0.3		-
Sulfur (ℓ)	43,500	32.06	1,358	-	x	x	x	x	43,500	x	x	310	0.2 Btu/lb °F	2.3	-	-
Waste Water (ℓ)	4,600	18.016	-	-	550	x	x	4,050	x	x	x	90	29.93 Btu/lb	0.1	x	x
㉓ **Vent Gas - SO_2 Absorber**																
SO_2	450	64.06	7	0.27	x	x	x	200	230	x	x	90	288 Btu/mol	x	x	x
N_2	72,650	28.02	2,593.5	99.39	x	x	72,650	x	x	x	x	90	194 Btu/mol	0.5	x	x
H_2O (v)	150	18.016	9	0.34	x	x	x	150	x	x	x	90	19,338 Btu/mol	0.2	x	x
Sub-Total	73,250		2,609.5	100.0	x	x	72,650	350	230	x	x			0.7		x
Sensible Heat Transferred to Gasifier Steam														854.3		
Sensible Heat to Cooling Water														108.4		
Heat of Reaction																
$CO + H_2O = CO_2 + H_2$ (851 mols x 1,430 Btu/mol)														1.2		
Heat Loss														+0.1		
Totals	5,316,700		-	-	129,600	751,250	2,780,300	1,600,200	45,100	1,800	8,450			3,499.4		

Note: Circled numbers refer to Stream Number on Consol Dwg. AP-3434. Temperature/Pressure may differ depending on location of identifying flag.

This defines, in dollar cost, the incentive to develop the hot clean-up technology. Both these cases are based on a regenerable sulfur acceptor as outlined in the section on experimental results. The economics of a once-through acceptor system are briefly explored in Case III.

In any case, the producer gas after expansion to 10 psig is delivered to the power station as preheated gas (540°F to 660°F). This sensible heat content serves to improve the efficiency (or the heat rate) of the station proper. In a conventional gas-burning station, the fuel gas is delivered at ambient temperature, and sensible heat from the products of combustion is recovered (via combustion air preheat) to an air heater exit temperature of about 300°F. It seems most realistic to credit the process with the excess sensible heat in the preheated producer gas above 300°F as an approximate means of measuring the improvement in the power station efficiency.

The sulfur removal facilities are arbitrarily identified as Section 300 (consistent with the numerical identification on Dwg. No. AF-3424), and the sulfur recovery facilities as Section 400. A conventional "hot pot" system to supply the required make-up CO_2 is labeled Section 500 although a detailed system design is not necessary.

The equipment required for the Venturi scrubbing system and the gas-gas heat exchangers are shown in Figure 3 and is identified as Section 600.

Plant and Operating Cost Estimates

Based on the experimental data obtained to date, a complete set of heat and material balances was developed for the entire process. These were discussed previously and are shown in Tables 4 through 10, inclusive. From these balances, a process flow sheet was developed as shown in Figures 3 and 4. A preliminary capital cost estimate was developed by the Consol Engineering Department for Sections 300, 400 and 600, and is summarized in tabular form in Appendix A as Tables A-1 through A-3, inclusive. Note that Section 500, the make-up CO_2 system was assumed to be a conventional "hot pot" system. A detailed estimate was not required since the costs and utility requirements are adequately defined in the literature.(12)

The capital cost estimates developed in Appendix A are defined as inside battery limits (ISBL). To these costs must be added off-site facilities (OSBL) which include utility costs, electric substations, cooling water towers, distribution piping, and boiler feed water treating. The accuracy of the capital cost estimates in this study is estimated as ± 20%.

It was required in this study to anticipate the escalation in these costs to a presumed start-up date of January, 1978. The economic climate at present defies a logical derivation of these factors. This work is based on these arbitrary assumptions:

1. July, 1973 costs as a base point.
2. Begin design and construction, January, 1974.
3. Begin operation, January, 1978.
4. Escalation at 7-1/2% per year average of construction labor and material.
5. Interest during construction at 7-1/2% simple interest on cash flow.
6. Escalation of direct operating labor at 5-1/2% per year.
7. Interest on working capital at 7-1/2% per year.

The total investment summary for the two cases described above is shown in Table 11. The installed plant cost (present day cost) for the "hot" gas clean-up scheme (Case I), is $34,800,000. The addition of product gas wet scrubbing with reheat adds $8,300,000 to the cost for a total of $43,100,000. Escalation of these costs to January, 1978 (as defined above) increases the total investment to $48,300,000 and $59,800,000, respectively. Most (approximately 70%) of the incremental cost of adding wet scrubbing with gas reheat is associated with the large gas-gas heat exchangers required.

Direct operating costs for these two cases were estimated as shown in Table 12. Note, that an average plant operating factor of 70% was assumed reflecting power station practice. The unit values used to develop operating costs are shown directly in Table 12.

Evaluation of System Economics

The previous report on this project(1) clearly showed that the most economic application of this process is in combination with a combined cycle power station. This current work is more restricted in scope and is limited to a simple exposition of the costs of desulfurizing the pressurized producer gas. Primarily the purpose is to focus attention on those areas where additional research and development work will be most valuable.

Based on the cost estimates presented in the above sections, the system costs are estimated as shown in Table 13. The net annual operating costs for Case I (hot cleanup) are $13,810,000 per year; for Case II (wet scrubbing with gas reheat), the costs are $17,081,000 per year. Approximately two-thirds of this cost is represented by capital charges. Note, that the low value for sulfur credit ($8.00/long ton) reflects a conservative view of the sulfur market.

Table 11

Investment Summary

Case	I				II	
Plant Section	300 Sulfur Removal	400 Sulfur Recovery	500 Make-up CO_2 System	Total	600 Product Gas Wet Scrubbing with Reheat	Total
Utilities Required						
Electricity, KW	2,490	10,030	344	12,864	512	13,376
Cooling Water, gpm	1,870	10,340	16,185	28,395	34,000	62,395
Low-Pressure Steam, lb/hr	x	x	78,300	78,300	x	78,300
Boiler Feed Water, gpm	x	1,234	x	1,234	x	1,234
Operating Labor Required						
Men/Shift	4	3	1	8	1	9
Investment	(in $1000)					
Erected Cost (ISBL)	15,000	11,400	3,900	30,300	6,600	36,900
Off-sites & Utilities (OSBL)						
Off-sites	1,200	900	200	2,300	500	2,800
Electrical	200	700	x	900	x	900
Cooling Water	x	400	600	1,000	1,200	2,200
Boiler Feed Water	x	300	x	300	x	300
Total OSBL	1,400	2,300	800	4,500	1,700	6,200
Installed Plant Cost (July, 1973)	16,400	13,700	4,700	34,800	8,300	43,100
Escalation to Jan. 1978				6,500		8,100
Sub-Total				41,300		51,200
Interest during Construction				7,000		8,600
Total Investment (Jan., 1978)				48,300		59,800

Table 12

Direct Operating Cost Summary
Excluding Acceptor Cost

Basis: 70% Plant Operating Factor

Case	I				II	
Plant Section	300 Sulfur Removal	400 Sulfur Recovery	500 Make-up CO_2 System	Total	600 Product Gas Wet Scrubbing with Reheat	Total
Direct Operating Labor						
Men/Shift	4	3	1	8	1	9
Direct Operating Cost				(in $1000/yr)		
1. Operating Labor at $63,200/man/shift/yr	253	190	63	506	63	569
2. Maintenance Labor at 1.6% Installed Plant Cost	262	220	75	557	133	690
3. Direct Supervision 15% of 1 + 2	77	61	21	159	30	189
4. Indirect Overhead 50% of 1 + 2 + 3	296	235	80	611	113	724
5. Payroll Overhead 15% of 1 + 2 + 3 + 4	133	106	36	275	51	326
6. Maintenance Material 2.4% Installed Plant Cost	394	328	113	835	199	1,034
7. Miscellaneous Supplies 15% Maint. Material	59	49	17	125	30	155
8. Utilities						
Electricity at 9 mills/KWH	138	553	19	710	28	738
Cooling Water at 3¢/M gal.	21	114	179	314	375	689
BFW at 30¢/M gal.	x	136	x	136	x	136
Low-Pressure Steam at 75¢/M lb	x	x	360	360	x	360
Chemicals & Catalysts (ex Acceptor)	x	x	13	13	x	13
Sub-Total Utilities	159	803	571	1,533	403	1,936
Totals	1,635	1,992	976	4,601	1,022	5,623
Escalation to Jan., 1978(1)				720		877
Total Direct Operating Cost (Jan. 1978)				5,321		6,500

(1) Items 2-7 are investment sensitive and are escalated on the same basis as plant investment. Items 1 and 8 are at assumed January 1978 values.

Table 13

Economic Evaluation
Regenerative Acceptor Desulfurization Process

Basis: 70% Plant Operating Factor (6132 hr/yr)

Case	I	II
Method of Producer Gas Clean-up (Particulate and Alkali)	Hot	Wet Scrubbing with Reheat
Coal Required:		
Tons/yr (6% Moisture)	3,422,000	
Higher Heating Value, MM Btu/yr	81.71×10^6	
Desulfurized Producer Gas to Station		
Mols/Hr	213,701	213,214
Temperature	660°F	540°F
Pressure	10 psig	10 psig
Higher Heating Value, MM Btu/yr	65.19×10^{12}	64.70×10^{12}
HHV + Sensible Heat Content, MM Btu/yr(1)	68.68×10^{12}	66.99×10^{12}
Cost Analysis		
Installed Plant Cost (1973)	$34.8 MM	$43.1 MM
Escalation to 1978	6.5 MM	8.1 MM
Interest during Construction	7.0 MM	8.6 MM
Total Investment	$48.3 MM	$59.8 MM
Working Capital	$ 1.33 MM	$ 1.63 MM
Annual Operating Costs		
Direct Operating Cost (1978 Basis)	$ 5.321 MM/Year	$ 6.500 MM/Year
Acceptor at $10/ton	0.648 MM/Year	0.648 MM/Year
Interest on Working Capital at 7.5%	0.100 MM/Year	0.122 MM/Year
Capital Charges at 18% Investment	8.694 MM/Year	10.764 MM/Year
Sulfur Credit at $8/metric ton	($ 0.953 MM/Year)	($ 0.953 MM/Year)
Net Annual Operating Cost	$13.810 MM/Year	$17.081 MM/Year
Desulfurization Cost Expressed:		
In terms of feed coal		
$/ton coal	4.03	4.98
¢/MM Btu HHV	16.9	20.9
In terms of product gas to station:		
¢/MM Btu HHV	21.2	26.4
¢/MM Btu (HHV + Sens. Ht.)(1)	20.1	25.4
Excess Power Generated by Expander	160 MW	118 MW

(1) Sensible heat content above an assumed air heater outlet temp. of 300°F.

In the cases where the acceptor is regenerated, the make-up acceptor cost has little impact on the system cost. Since this study does not define a specific plant site, a definitive cost for delivered acceptor cannot be derived. An arbitrary cost of $10.00 per ton of raw stone ($MgCO_3CaCO_3$) was assumed. This somewhat high cost is based on two facts: a) the laboratory studies to date have shown that some dolomitic stones cannot be used in the process (excessive attrition) thereby limiting the potential supply sources, and b) transportation costs for raw materials are substantially increasing. However, even with an acceptor make-up cost of $10.00 per ton, the annual cost is only 4-5% of the total system cost. The imprecision of the acceptor cost has only a minor influence on the evaluation of the total system.

The system costs presented in Table 13 are more meaningful if related to either the coal required for the system, or to the quantity and quality of the gas delivered to the power station. The net annual operating costs for Case I are equivalent to $4.03 per ton of feed coal; for Case II, $4.98 per ton. Expressed in terms of heating value of the coal, the corresponding costs are 16.9 and 20.9¢/MM Btu, respectively.

Considering only the higher heating value of the product gas to the power station, the corresponding costs are 21.2 and 26.4¢/MM Btu for Cases I and II, respectively. Allowing for the sensible heat credit discussed earlier, the costs are reduced to 20.1 and 25.4¢/MM Btu, respectively. Note, that the sensible heat credit reduces the process cost by about 4-5%. The addition of wet scrubbing and gas reheat increases the processing cost by 5.3¢/MM Btu or 26%.

As discussed earlier, another credit to the process is the excess power generated by the expanding turbine-generator set. For Case I this amounts to 160 MW; for Case II, 118 MW. As noted previously, it is beyond the scope of this contract to evaluate the dollar credit associated with this excess power. However, the impact of the credit upon the processing costs can be at least qualitatively defined. The real cost of electric power generated by an expanding turbine-generator set would normally be less than steam-generated power. If the real cost were one mill/KWH less, then the credit to the process would be for Case I, 1.5¢/MM Btu, and for Case II, 1.1¢/MM Btu. These are significant credits, but could only be evaluated with accuracy through a detailed study.

Non-Regenerable Acceptor

The basic development of this project to date has been devoted to the concept of a regenerable sulfur acceptor. The feasibility of this concept has been discussed earlier in the review of the experimental data. As pointed out in the previous section, modest (1-2%) make-up acceptor requirements in the regenerative case do not significantly influence the process costs. However, this would not be true for a non-regenerable or once-through system. In a once-through acceptor system, approximately fifteen times as much raw stone is required. This is shown in Table 14.

In the once-through acceptor system, the recovery of sulfur would be somewhat simplified. All of the sulfur removed from the producer gas would be recovered by stripping the spent acceptor with water and a CO_2-bearing gas stream. The acid gas from this system would then be fed to a standard Claus plant for recovery of elemental sulfur. However, the spent acceptor stripping system would have to be expanded to handle a fifteen-fold increase in spent acceptor flow, and the make-up CO_2 requirements (to convert MgOCaS to $MgCO_3CaCO_3$) would also increase fifteen-fold.

Table 14

Acceptor Requirements
Regenerative vs. Once-Through

Basis: 70% Plant Operating Factor (6132 hours/year)

Case	I	III
Method	Regenerative Acceptor Hot Gas Cleanup	Once-Through Acceptor Hot Gas Cleanup
Coal Required:		
Lb/hr (6% Moisture)	← 1,116,150 →	
Tons per year (6% Moisture)	← 3,422,000 →	
Higher Heating Value, MM Btu/Year	← 81.71×10^{12} →	
Acceptor Required:		
Mols Ca Circulating/Hour	10,504	1,598
Mols Make-up Ca/Hour	105	1,598
Make-up Acceptor ($MgCO_3CaCO_3$):		
Lb/Hr	21,150	321,900
Tons/Year	64,850	986,900
Annual Cost of Make-up Acceptor at $10/Ton	$648,500	$9,869,000

The maximum savings would accrue if a naturally CO_2-rich stream could be used which would obviate the need for a CO_2 recovery step. Power station stack gas with a CO_2 concentration of about 15 volume percent is a speculative possibility here. The maximum potential savings in investment on this assumption is approximated as about $10 MM. This is detailed in Table 15 below:

Table 15

Approximate Investment Reduction
Once-Through Acceptor vs. Regenerative

Case	I Regenerative Acceptor Hot Gas Cleanup	III Once-Through Acceptor Hot Gas Cleanup
Installed Cost by Section	(Table 11)	
Section 300 - Sulfur Removal	$ 16.4 MM	$ 20.5 MM
Section 400 - Sulfur Recovery	$ 13.7 MM	$ 4.2 MM(1)
Section 500 - Make-up CO_2	$ 4.7 MM	$ 3.1 MM(2)
Total	$ 34.8 MM	$ 27.8 MM
Escalation & Interest During Construction	$ 13.5 MM	$ 10.8 MM
	$ 48.3 MM	$ 38.6 MM

(1) Split-flow Claus plant.
(2) Compression cost only - No CO_2 absorption step.

At an 18% capital charge, the annual saving from the investment reduction of about $10 MM would be $1,800,000 per year as opposed to an annual increase in acceptor make-up cost of about $9,200,000 per year. On this basis we conclude that there is no incentive to explore further the once-through acceptor case.

This conclusion is based on the requirement that the MgOCaS from the process must be converted to $MgCO_3CaCO_3$ for disposal. Alternatively, the MgOCaS might be converted to $MgOCaSO_4$ by high-temperature oxidation. However, our limited data show that the spent CaS is difficult to oxidize and that SO_2 is formed. Disposal of $CaSO_4$ may create a water pollution problem in some areas.

IV. EQUIPMENT AND PROCEDURE

A. Description of the Continuous Unit

1. Process Piping and Equipment

A simplified flow diagram of the continuous acceptor reaction loop is shown in Figure 5. A more detailed process and instrumentation diagram is shown in Figure 6. These figures show the unit as arranged for operation where the acceptor is recirculated continuously between the gas desulfurizer and regenerator reactor. The following description applies to the above system. For operation of a single vessel, the equipment and procedure, in general, are the same as described here. The differences which are entailed in operation of a single vessel are detailed in part C of this section.

2. Process Vessels

The D-2 gas desulfurizer vessel, as shown in Figure 7, is three inches in diameter. The acceptor bed height was maintained 18 inches by means of a d/P level controller.

The D-1 regenerator vessel, shown in Figure 8, is two inches in diameter, and the bed height was maintained at 46 inches. The upper portion of the vessel was enlarged to 4 inches to allow for additional internals above the bed.

Heat was supplied through the walls of the process vessels. The regenerator heater contained three separate circuits which corresponded to the bottom, middle and top zones of the reactor. The gas desulfurizer was equipped with four heater circuits spaced along the length of the reactor. All the regenerator heaters and the top zone gas desulfurizer heater were controlled by 270 volt Powerstats supplying 5.1 KW of electrical heat. The three lower heaters on the gas desulfurizer were controlled by 230 volt Powerstats supplying 3.8 KW.

The process vessels and their heaters were contained in pressure shells which were pressurized with CO_2, so that the pressure drops across the walls of the process vessels are zero. Both pressure shells were detailed earlier.(1)

Johns-Manville Sil-O-Cel C-3 insulation was used to fill the annular space between the heaters and the wall of the gas desulfurizer pressure shell. The gas desulfurizer pressure shell wall temperature was held below 950°F. The annular space between the heaters and wall of the regenerator pressure shell was filled with Carborundum "Fiberfrax" insulation. The regenerator pressure shell wall temperature was held below 700°F.

3. Solids Handling

Acceptor was handled in three streams, regenerated acceptor from the regenerator, regenerated acceptor to the gas desulfurizer, and sulfided acceptor to the regenerator.

The regenerated stone was fed to the top of the gas desulfurizer bed in an electrically heated pneumatic transfer line. The sulfided stone was drained from the bottom of the gas desulfurizer into a purged standleg L-5, which formed the seal between the gas desulfurizer and regenerator.

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The sulfided acceptor entered the top flange of the regenerator, and passed through a preheater purged with CO_2 which was introduced into the acceptor return line above the vessel. The preheater was a stainless steel tube, 7/8" OD x 3/4" ID x 10" long having nine baffles installed at 60° angles.

Acceptor from the regenerator was withdrawn through a standleg into one of two lockhoppers, F-6A and F-6B, at a rate dictated by the level of the bed. The acceptor was removed from the off-stream lockhopper and charged back to one of two acceptor feed hoppers, F-4A or F-4B. Continuity of acceptor circulation was maintained by feeding acceptor to the regenerator alternately from the two feed hoppers. A sight glass was installed below the feed hoppers to show when the on-stream feed hopper was empty. The feed hoppers and withdrawal hoppers each had a capacity of six pounds of raw acceptor.

A sampling valve was inserted in the L-5 acceptor return line through which a sample of sulfided acceptor could be diverted into a sampling cylinder while the unit was operating.

Sulfided acceptor and acceptor from the regenerator were conveyed by gravity flow in purged standlegs. These standlegs were purged with inert gas to prevent steam from either vessel from getting in and condensing in a cold spot. The solids flow rates were controlled to maintain the standlegs full of solids. To protect the Teflon seats in the valves used to control the solids flow rates, water-jacketed coolers were installed in each of the standlegs. These coolers were detailed earlier.(1,3) Sight glasses (Jerguson 12-T-20) were also installed in each standleg to allow visual confirmation of the amount and nature of solids flow.

4. Gas Flows

The gas desulfurizer inlet gas consisted of recycled product gas with N_2, H_2S, H_2, CO_2, and steam flows added to give the desired gas composition.

The metered dry desulfurizer fluidizing gas was passed through the steam generator which is shown in Figure 9. The water temperature in the steam generator was controlled (± 0.5°F) to give the desired steam partial pressure. Calibrations showed that at water temperatures we used, the steam partial pressure was equal to the equilibrium vapor pressure of water. The steam generator feed water was passed through a Barnstead demineralizer.

The fluidizing gas passed through an electrically heated line from the steam generator to the top of the desulfurizer. The wall temperature in the line was kept above 400°F to prevent condensation of the steam. The gas inside the gasifier vessel passed through a helically-wound preheat coil and an axial dip tube which extended into a cone at the bottom of the vessel. The gas passed downward, reversed direction, and fluidized the bed. The pneumatic lift gas entered the top of the vessel, disengaged from solids, and exited with the fluidizing gas.

The desulfurizer outlet gas passed through one of two parallel filters where solids carried over from the gasifier bed were removed using F-porosity Micro-Metallic filters. Both of the filters and the upstream piping were heated electrically to prevent condensation of steam in the outlet gas. Separate heating circuits were provided for each of the filters so that they could be cooled before being removed for cleaning and heated rapidly after being reinstalled.

Steam was condensed in the C-7 cooler and collected in the F-7 condensate receiver. These are detailed in Figures 10 and 11, respectively. The gas was further cooled in the C-6 cooler using chilled water at 40°F.

The dry, solids-free desulfurizer product gas was vented to atmospheric pressure through the back pressure control valve DPCV-1.

The regenerator inlet gas consisted of CO_2 and steam with air or hydrogen sometimes added. The gas entered the top of the regenerator and passed through a helically-wound preheat coil and an axial dip tube which extended into the cone at the bottom of the vessel. The gas passed downward, reversed direction, and fluidized the bed. In the electrically heated exit piping, solids were removed in one of two parallel filters which used F-porosity Micro-Metallic filter elements.

The unreacted steam was condensed in the C-1 cooler. The condensed steam was collected in the condensate receiver F-8 which was mounted below C-1. A liquid level controller actuated a control valve LCV-5 to drain condensate and maintain a constant liquid level in the receiver.

The gas was further cooled in the C-4 cooler using water supplied at 40°F from a water chilling unit. Additional condensate was disengaged in knock-out pot F-9 and collected in the sight glass below F-9.

The dry, solids-free product gas was vented to atmospheric pressure through the regenerator back pressure control valve PCV-1.

Small metered flows of N_2 were used to purge the pressure taps at the tops of both vessels as well as the L-6 standleg in the acceptor return line while the L-5 standleg was purged with CO_2. All of the purge flows were as small as possible relative to the fluidizing gas flows.

The H_2, CO_2, and N_2 used as process gas, pressure shell balance gas, and lockhopper pressurizing gas were supplied from cylinders. Regulators downstream of the cylinder manifolds fixed the supply pressures at 300 psig. Air was supplied from a compressor. Water and oil were removed by a knock-out drum followed by a bed of silica gel. C.P. grade hydrogen sulfide was supplied from cylinders. At 15 atmospheres, hydrogen sulfide is close to its liquid point, and therefore cannot be fed reliably as a gas. Therefore, the cylinder of liquid H_2S was turned upside down so that the H_2S could be fed as a liquid. The cylinder was kept in a compartment thermostated at 90°F to give about 300 psig over the liquid. The H_2S feed system is shown schematically in Figure 12.

Identical single-stage diaphragm compressors (Pressure Products Industries, Model No. 1073) were used to recycle product gas.

5. Miscellaneous Piping

Wherever possible, connections to the process piping were high-pressure coned fittings (Autoclave Engineers or Pressure Products) which were used because of their ruggedness, ease of disassembly, and freedom from leaks.

Special adapter fittings were required to connect the solids outlet tubes (3/8" x .035" wall) to the standleg piping (9/16" OD x 5/16" ID). The solids outlet tubes from the vessels slipped inside the adapter fittings and were sealed using a lava sealant and packing gland. A standard high-pressure connection was made between the adapter fitting and the standleg.

In order to minimize the pressure drop across the gas outlet piping, 3/8" x .028" wall tubing was used downstream of C-1 and C-6 coolers in the gasifier and regenerator, respectively.

The steam condensate contained dissolved NH_3, SO_2, H_2S, and CO_2. Types 304 and 316 stainless steel gave excellent service in piping and equipment handling process gases at temperatures from ambient to 400°F. Previous experience had shown that condensate and wet process gases are extremely corrosive to copper, brass and plain carbon steel. These materials were not used, even in the instrumentation piping.

Conax packing glands and lava sealants were used where the heater leadwires, solids outlet tubes, and the vessel skin thermocouples passed through the pressure shells.

6. Pressure Measurement and Control

The system pressure was controlled at the top of the regenerator vessel using a Foxboro pressure cell and recorder-controller which operated the back pressure control valve PCV-1. The pressure at the top of the gas desulfurizer was maintained at a fixed differential (usually in the range of zero to five inches H_2O) from that at the top of the regenerator using a Foxboro d/P cell, and a recorder-controller which operated the desulfurizer back pressure control valve DPCV-1.

The discharge pressures of the two recycle compressors were controlled using Foxboro indicator controllers which operated control valves PCV-2 and PCV-3 and which vented to the suction side of the compressors.

Identical balance gas systems were used to maintain a zero pressure differential across the walls of both process vessels. CO_2 was supplied to the pressure shell at 300 psig. Barton d/P cells and recorder-controllers operated control valves DPCV-11A and 11B and DPCV-13A and 13B which either loaded the shell or vented CO_2 to the atmosphere to maintain a zero pressure differential between the pressure shell and the process vessel.

The unit was adequately instrumented to monitor pressure drops across the various transfer lines, standlegs, and fluidized beds. These pressure drops were measured with respect to the pressures at the top of the gas desulfurizer or regenerator vessels, and were continuously recorded.

The pressure drops across the solids filters in both the gas desulfurizer and regenerator outlet gas piping were continuously recorded. The filters were switched when the pressure drop across the on-stream filter reached 75" of H_2O.

Panel mounted pressure gauges were used to indicate the pressures at the top of both vessels, the pressure shell pressures, the compressor discharge pressure and the pressures immediately upstream of the back pressure control valves. Locally mounted pressure gauges were used to indicate the pressures in the steam generators and the various lockhoppers.

7. Temperature Measurement and Control

The bed temperature in both the gas desulfurizer and regenerator were measured using chromel-alumel thermocouples contained in wells which were immersed in the fluidized beds. Two thermocouples were used in the regenerator thermowell and one in the gas desulfurizer.

The bed temperatures were controlled manually by adjusting the Powerstats which controlled the electrical heat input from the heaters.

In each vessel, the wall temperatures corresponding to each of the heating zones were measured using thermocouples which were inserted through the side of the pressure shell and through slots ground in the heater ceramics.

The water temperature in each steam generator was monitored using an Iron-Constantan thermocouple contained in an axial thermowell. The thermocouple signal was recorded using a Foxboro temperature recorder-controller. A high or low temperature activated relay which supplied power to the steam generator bayonet heater from the appropriate one of two 7.5 KW Powerstats which were set by trial to supply slightly more and slightly less than the required steady-state input.

Up to 28 temperatures were monitored of which 26 could be continuously recorded. The other temperatures included the wall temperatures of the pressure shells, the transfer lines, the inlet and outlet gas piping, the steam generators, and solids filters. Thermocouples inserted in the sight glasses in the various standlegs monitored the temperatures of the solids flowing from the water-jacketed coolers.

8. Control of Solids Flow Rates

The solids feed rates were controlled using rotary feeders which consisted of a tapered Teflon plug rotating inside a stainless steel body. Drawings of the feeders used in the continuous unit were shown earlier.(1,3) The number, diameter, and depth of the pockets were chosen on the basis of the bulk density of the solids and the desired range of solids flow rates. Variation of the solids flow rates over the desired range was accomplished by means of a Graham variable speed drive. Slots were milled in the feeder body around the inlet and outlet ports to allow the pockets to begin to fill and discharge before reaching top and bottom dead center. Since Teflon was used, no lubrication was required between the feeder body and rotor.

The flows of solids in the L-5 and L-6 standlegs were controlled by air-operated Contromatics ball valves having a 7/16" bore. The opening and closing of the valves was determined by the level control system as discussed below.

9. Solids Level Control

Level control in both vessels was regulated by means of differential pressure measurements. In the gas desulfurizer, a d/P measurement was made between the top of the vessel and a point two inches below the desired bed height. The corresponding points in the regenerator were the top of the vessel and a point four inches below the desired bed height.

At our operating conditions each inch of coverage of the bed pressure probe produced about 3/4" of water of pressure drop. The pressure drop was changed into a 3-15 psi signal through a pressure transducer. The latter signal in turn operated pressure switches connected to solenoid selector valves which supplied air at one of three preset pressures to a Conoflow cylinder operator. This adjusted the opening of the ball valve in the appropriate standleg.

The operation of both the L-5 and L-6 valves was monitored continuously by recording the air pressure supply to the Conoflow cylinder operator. The height of bed above the pressure tap was monitored by recording the output pressure of the pressure transducers.

10. Gas Flow Measurements

The inlet gas flows were metered using rotameters which were calibrated with either a Rockwell dry gas meter or a wet test meter depending on the range of the rotameter. The gas meters were calibrated against a volume meter using displacement of a mercury sealed piston accurate to 0.2%.

Rotameters using recycle gas were calibrated using two gases having different molecular weights. The flow rates were correlated with the rotameter float heights using the following general equation:

$$Q = C_o + \frac{C_1 \times S}{(MW)^{.5}} + \frac{C_2 \times S^2}{(MW)^{.5}}$$

Where: Q = flow rate, SCFH.
S = float height.
MW = molecular weight of the recycle gas.
C_o, C_1, C_2 = constants for a given rotameter determined via regression analysis.

The recycle rotameters were calibrated with H_2 and N_2 at a supply pressure of 300 psig.

The dry product gas flow rates from both vessels were measured using calibrated Rockwell dry gas meters located downstream of the back pressure control valves.

11. Gas Analysis

The product gas streams from both vessels were analyzed using a gas chromatograph. During a run, low levels of CO, CO_2, and SO_2 were continuously monitored with infrared analyzers. High levels of CO_2 were monitored with a thermal conductivity cell with reference to nitrogen. A paramagnetic susceptibility analyzer was used to measure the concentration of oxygen. The outputs of the CO, CO_2, SO_2, and O_2 analyzers and of the thermal conductivity cell all were continuously recorded. Analyses were made on the gas chromatograph when the above analyzers indicated that the gas composition was steady.

All of the gas analysis instruments were connected to manifolds so that offgas from either the regenerator or gas desulfurizer could be fed to each. For integrated operation, the chromatograph analyzed both the regenerator and gas desulfurizer offgases. In addition, gas samples were taken into a stainless steel cylinder for intensive chromatographic analysis by the analytical laboratory.

Hydrogen sulfide was to be measured with an infrared analyzer, but the performance of the instrument was not satisfactory. Instead H_2S from both vessels was determined using a standard type of iodine method.(13)

12. Safety Features

The unit was equipped to give an audible alarm whenever a potentially dangerous upset occurred. A light indicating the source of the upset accompanied an alarm. In some situations, relays were activated which closed the emergency solenoid valve to isolate the gas desulfurizer and regenerator vessels and shut off appropriate solids feeders.

If steam were to condense in the L-5 standleg, the acceptor would become a solid plug. During normal operations, cross-contamination was prevented by maintaining the CO_2 purged standleg above the L-5 valve full of acceptor and by controlling the pressure differential between the top of the gas desulfurizer and regenerator vessels such that the pressure drop across the L-5 valve was zero. If an upset occurred such that the pressure differential between the vessels deviated ± 10" H_2O from the set valve or the pressure drop across the L-5 valve deviated ± 5" H_2O from zero, an alarm sounded and the emergency solenoid valve closed, thereby isolating the gas desulfurizer and regenerator vessels.

Recycle gas was used to transport acceptor to the gas desulfurizer and was a major constituent of the fluidizing gases. Pressure switches were installed to sound an alarm, close the emergency solenoid valve, and shut off the L-4 feeder if the discharge pressure of the recycle gas compressor fell below a preset value.

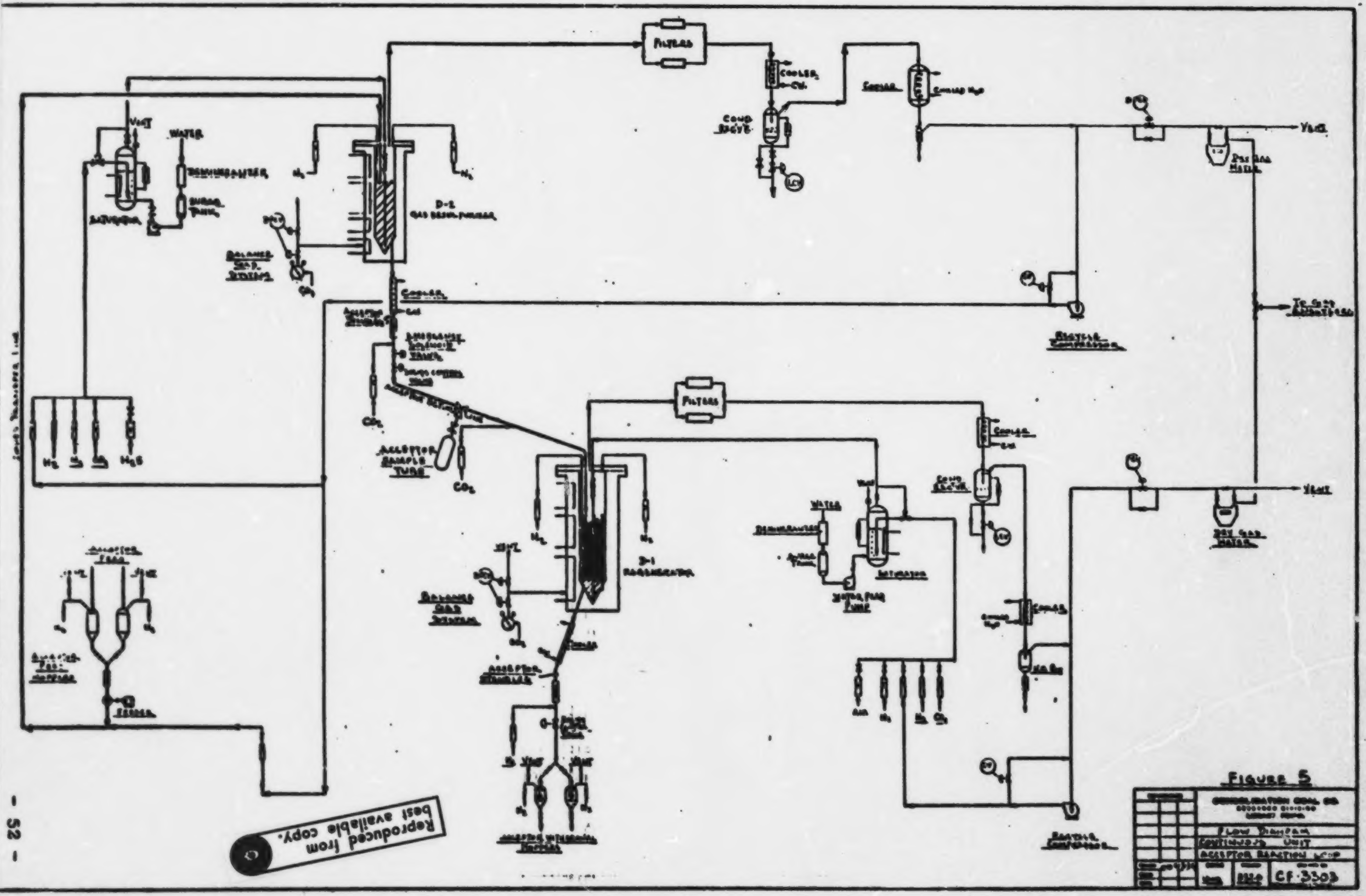
The supply of acceptor was monitored using alarms. High and low ΔP alarms were installed to detect plugging or starvation in the acceptor transfer line.

The unit was equipped with a high ΔP alarm to detect plugging in the gas desulfurizer inlet piping. Another alarm sounded in the event of malfunctioning of the back pressure valve or of plugging in the gas desulfurizer outlet piping, as indicated by a high pressure at the top of the vessel. Other alarms warned of malfunction of the liquid discharge valve below the condensate receiver, as indicated by a high or low condensate level.

Failure of the balance gas system to control pressure differential across the walls of either process vessel could have resulted in collapse or rupture of the vessel. An alarm was provided to indicate any deviation in the pressure differential between either process vessel and its pressure shell greater than 25" of H_2O and another alarm was used to indicate a low pressure in the CO_2 cylinder manifold which supplied the balance gas.

Nitrogen was available to supply pressure to the instruments if the supply of instrument air were lost, as shown by an alarm indicating low instrument air supply pressure. If cooling water from the cooling tower were cut off, as indicated by a low pressure alarm, water was available from the city water supply.

The H_2S feed system was equipped with high and low pressure alarms and relief valves which vented to an afterburner. During operations, the air was continually sampled for its H_2S concentration with MSA "sniffer" tubes.



VENT
WATER
DEMINERALIZER
SURGE TANK
SATURATOR
BALANCE GAS SYSTEM
D-2
COOLER
FILTERS
COND. RECV'R
CHILLED H2O
RECYCLE COMPRESSOR
DRY GAS METER
TO GAS ANALYZERS
ACCEPTOR SAMPLE TUBE
CO2
N2
H2S
D-1
REGENERATOR
WATER FEED PUMP
ACCEPTOR FEED
FEEDER
ACCEPTOR STANDLEG
ACCEPTOR WITHDRAWAL HOPPERS
FLOW DIAGRAM
CONTINUOUS UNIT
ACCEPTOR REACTION LOOP
CF-3303

FIGURE 5

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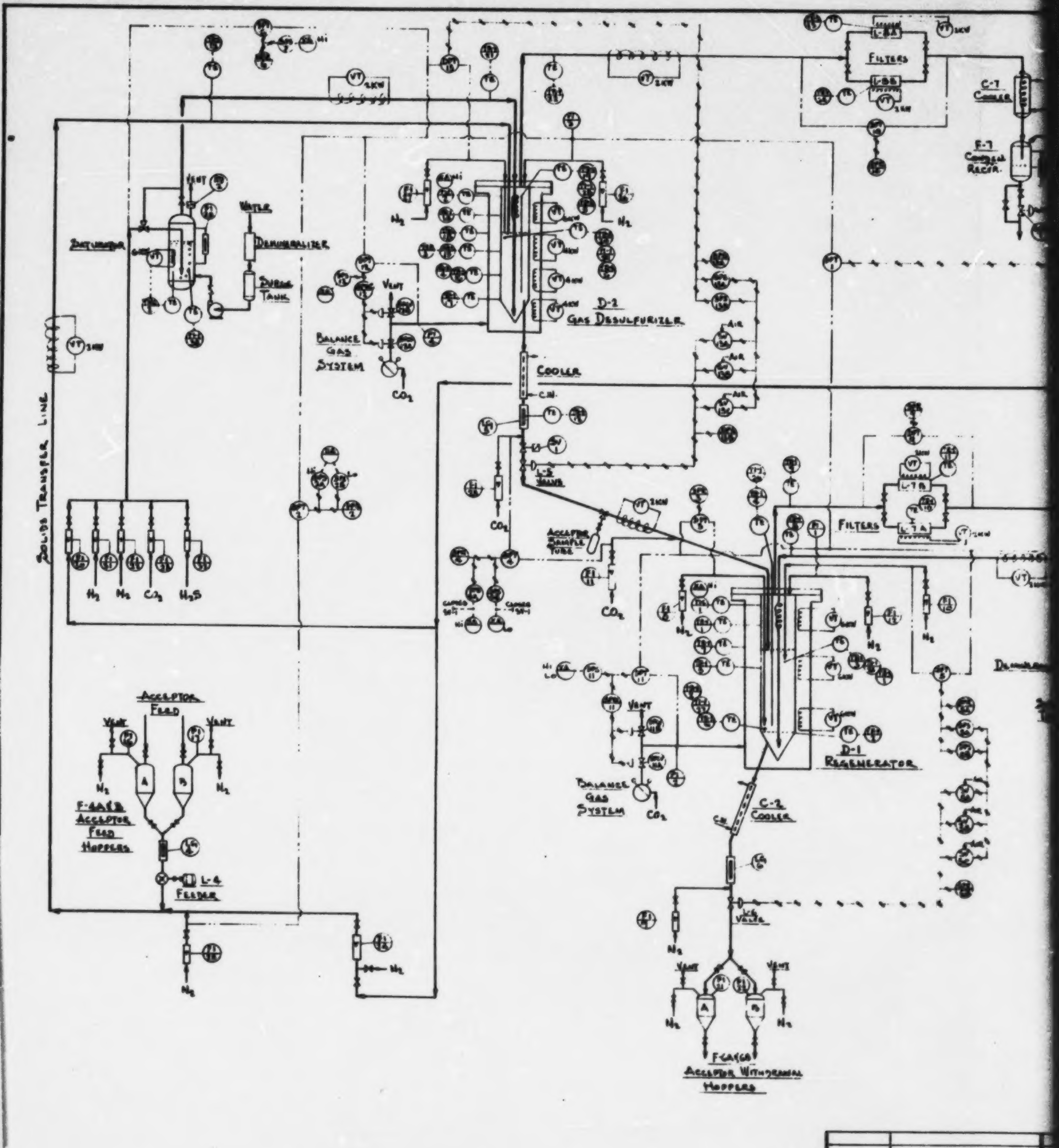

Saturator
Vent
Water
Demineralizer
Surge Tank
VT 2KW
Solids Transfer Line
N_2
N_2
CO_2
H_2S
Balance Gas System
CO_2
D-2
Gas Desulfurizer
N_2
Cooler
C.W.
L-5 Valve
Air
Air
Air
Filters
L-8A
L-8B
VT 2KW
C-7 Cooler
F-7 Condensate Recvr.
Acceptor Sample Tube
Filters
L-7A
L-7B
Hi
Lo
Vent
Balance Gas System
CO_2
D-1
Regenerator
C-2
Cooler
C.W.
L-6 Valve
N_2
Acceptor Feed
Vent
Vent
A
B
N_2
N_2
F-4A&B
Acceptor Feed Hoppers
L-4 Feeder
N_2
N_2
Vent
Vent
A
B
N_2
N_2
F-6A&B
Acceptor Withdrawal Hoppers

A

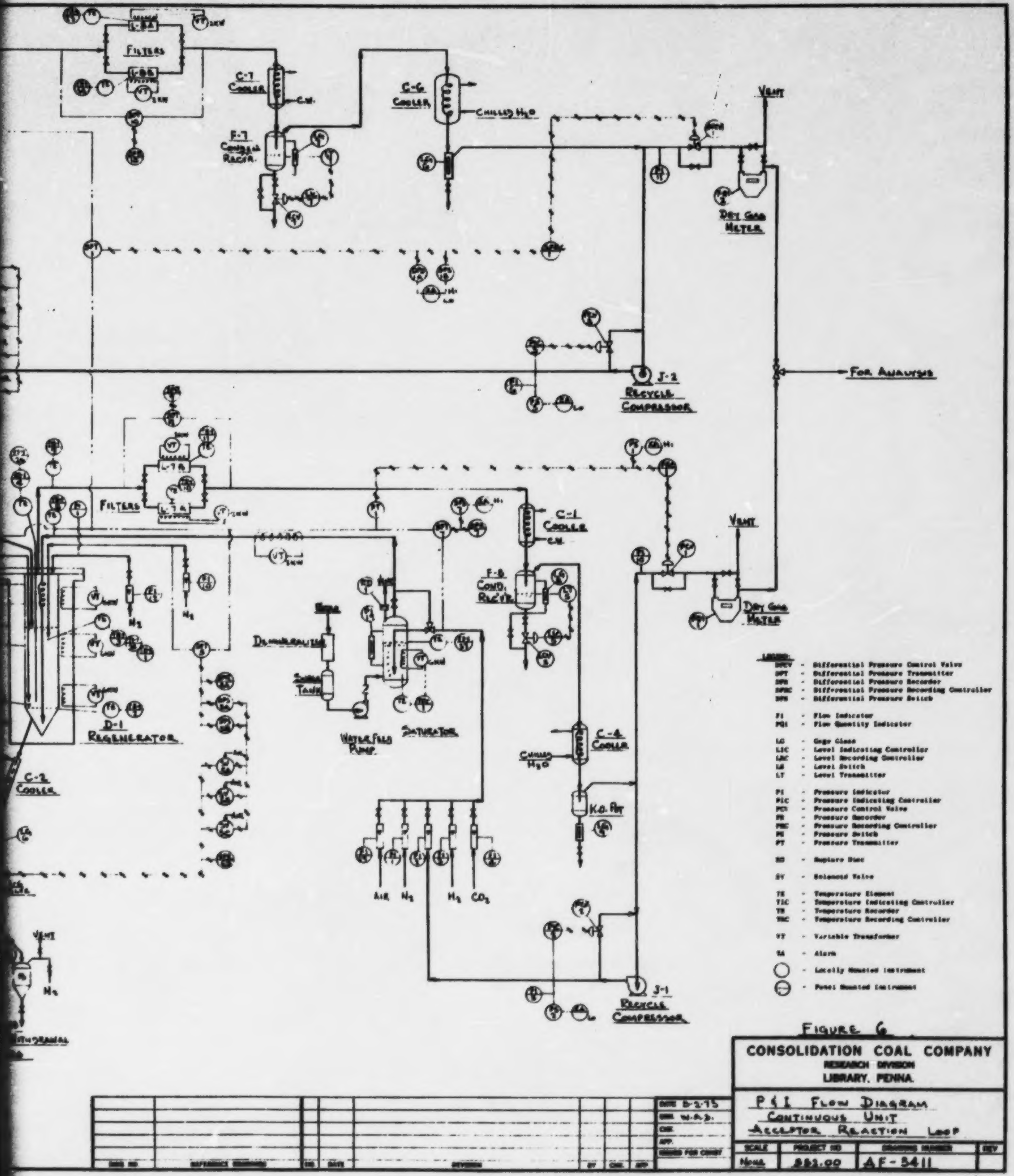
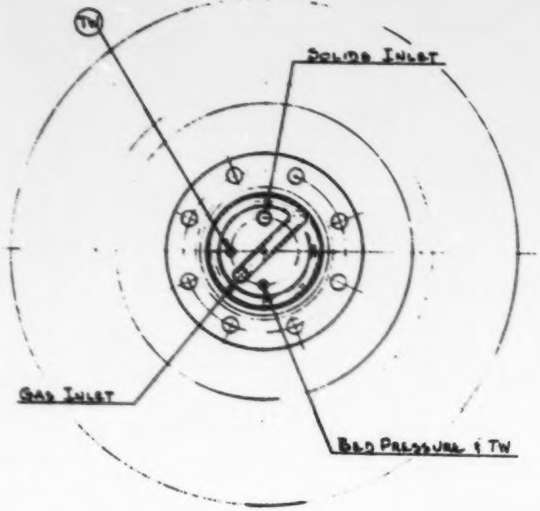
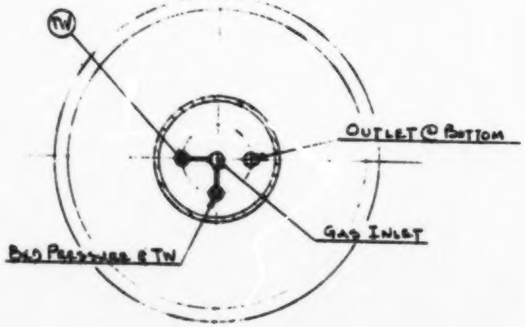

Filters
C-7 Cooler
C.W.
C-6 Cooler
Chilled H2O
F-7 Condensate Receiver
Vent
Dry Gas Meter
J-2 Recycle Compressor
For Analysis
Filters
C-1 Cooler
C.W.
F-8 Cond. Rec'vr.
Vent
Dry Gas Meter
Demineralizer
Surge Tank
Water Feed Pump
Saturator
D-1 Regenerator
C-2 Cooler
C-4 Cooler
Chilled H2O
K.O. Pot
Air
N2
H2
CO2
N2
J-1 Recycle Compressor
Vent
N2
Withdrawal
Legend:
DPCV - Differential Pressure Control Valve
DPT - Differential Pressure Transmitter
DPR - Differential Pressure Recorder
DPRC - Differential Pressure Recording Controller
DPS - Differential Pressure Switch
FI - Flow Indicator
FQI - Flow Quantity Indicator
LG - Gage Glass
LIC - Level Indicating Controller
LRC - Level Recording Controller
LS - Level Switch
LT - Level Transmitter
PI - Pressure Indicator
PIC - Pressure Indicating Controller
PCV - Pressure Control Valve
PR - Pressure Recorder
PRC - Pressure Recording Controller
PS - Pressure Switch
PT - Pressure Transmitter
RD - Rupture Disc
SV - Solenoid Valve
TE - Temperature Element
TIC - Temperature Indicating Controller
TR - Temperature Recorder
TRC - Temperature Recording Controller
VT - Variable Transformer
SA - Alarm
○ - Locally Mounted Instrument
⊖ - Panel Mounted Instrument
CONSOLIDATION COAL COMPANY
RESEARCH DIVISION
LIBRARY, PENNA.
P & I Flow Diagram
Continuous Unit
Acceptor Reaction Loop
DATE 5-2-75
DWN. W.A.S.
CHK.
APP.
ISSUED FOR CONST.
SCALE None
PROJECT NO. 862.00
DRAWING NUMBER AF-3411
REV
DWG NO
REFERENCE DRAWINGS
NO.
DATE
REVISION
BY
CHK.
APP.

Figure 6

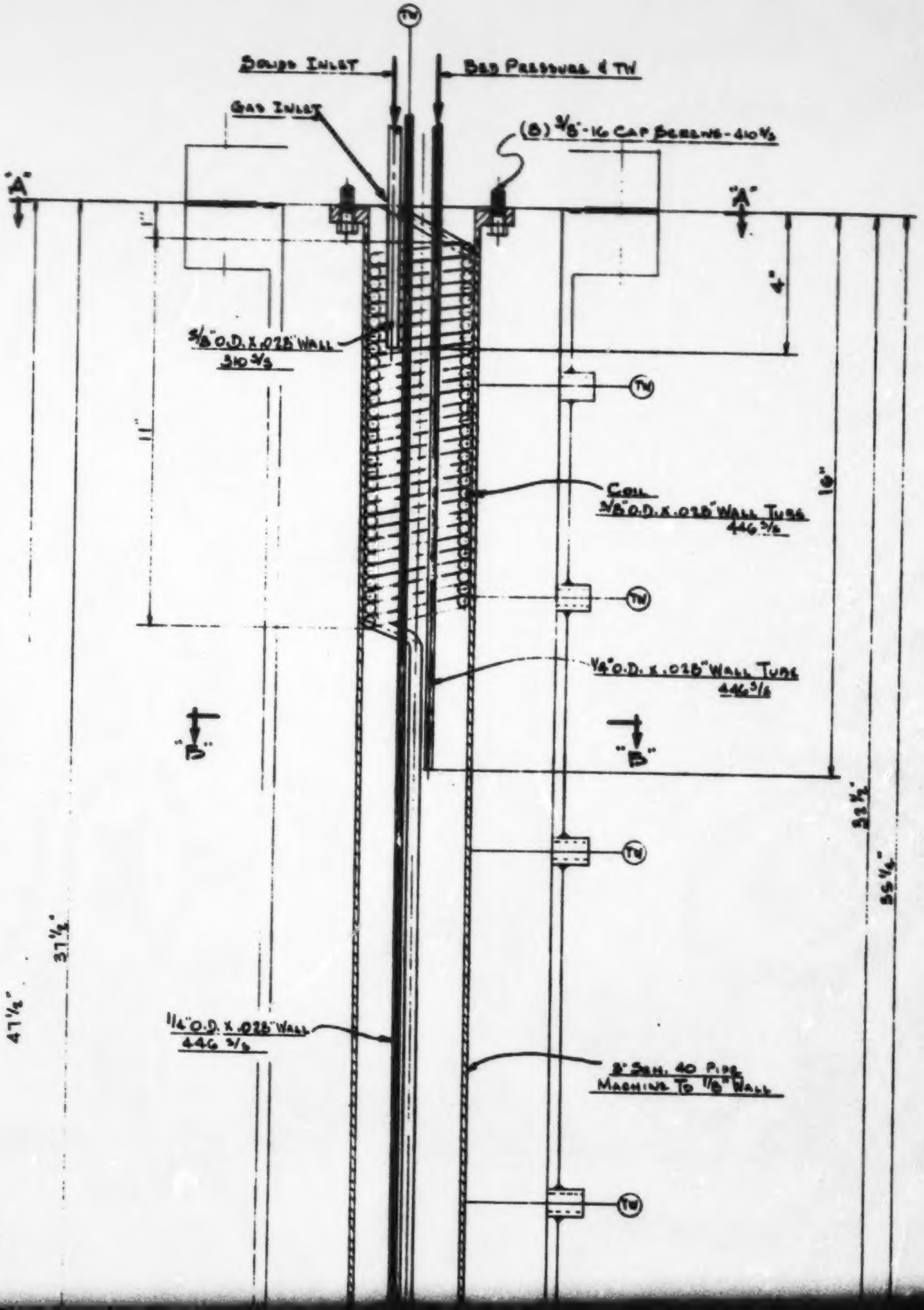
B

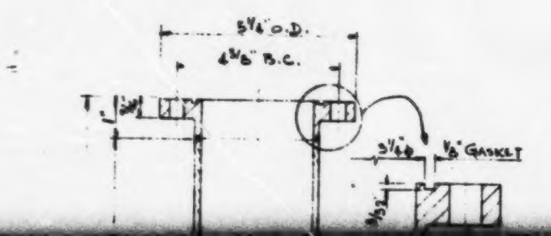

TW
Solids Inlet
Gas Inlet
Bed Pressure & TW

~SECTION "A-A"~


TW
Outlet @ Bottom
Gas Inlet
Bed Pressure & TW

~SECTION "B-B"~


TW
Solids Inlet
Bed Pressure & TW
Gas Inlet
(8) 3/8"-16 Cap Screws-410 S/S
"A"
"A"
1"
4"
11"
16"
5/8" O.D. x .028" Wall
310 S/S
Coil
3/8" O.D. x .028" Wall Tube
446 S/S
1/4" O.D. x .028" Wall Tube
446 S/S
"B"
"B"
33 3/4"
55 3/4"
37 1/2"
47 1/2"
1 1/4" O.D. x .028" Wall
446 S/S
8" Sch. 40 Pipe
Machine to 1/8" Wall
TW
TW
TW
TW


5 1/4" O.D.
4 3/8" B.C.
T
3/4
3 1/64
1/8" Gasket
3/32

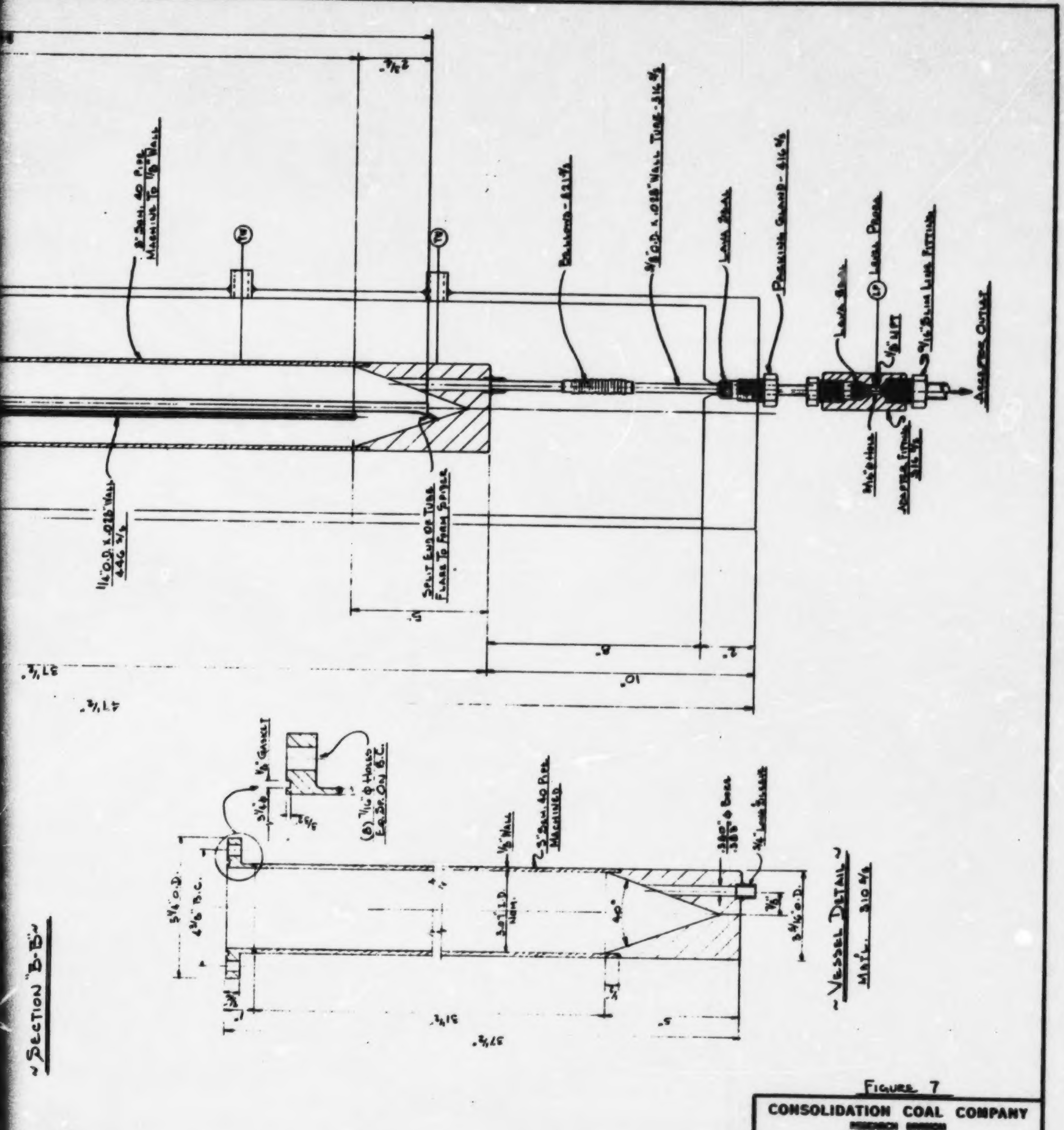

8" SCH. 40 PIPE MACHINE TO 1/8" WALL
TW
TW
BELLOWS - 321 S/S
3/8" O.D. x .028" WALL TUBE - 316 S/S
LAVA SEAL
PACKING GLAND - 316 S/S
LAVA SEAL
LP LAVA PROBE
1/8" NPT
9/16" BLIND LINE FITTING
ANALYZER OUTLET
9/16" Φ HOLE
ADAPTER FITTING 316 S/S
SPLIT END OF TUBE FLARE TO FORM SPIDER
1 1/4" O.D. x .028" WALL 446 S/S
5"
8"
2"
10"
37 1/4"
37 1/4"
(8) 7/16" Φ HOLES EQ. SP. ON B.C.
1/8" GASKET
3" SCH. 40 PIPE MACHINED
1/8" WALL
5 1/4" O.D.
4 3/4" B.C.
3.07" I.D. NOM.
40°
.380"/.385" Φ BORE
3/4" LONG SLEEVE
3 1/2" O.D.
5"
31 1/4"
37 1/4"
VESSEL DETAIL
MAT'L. 310 S/S
SECTION "B-B"

FIGURE 7

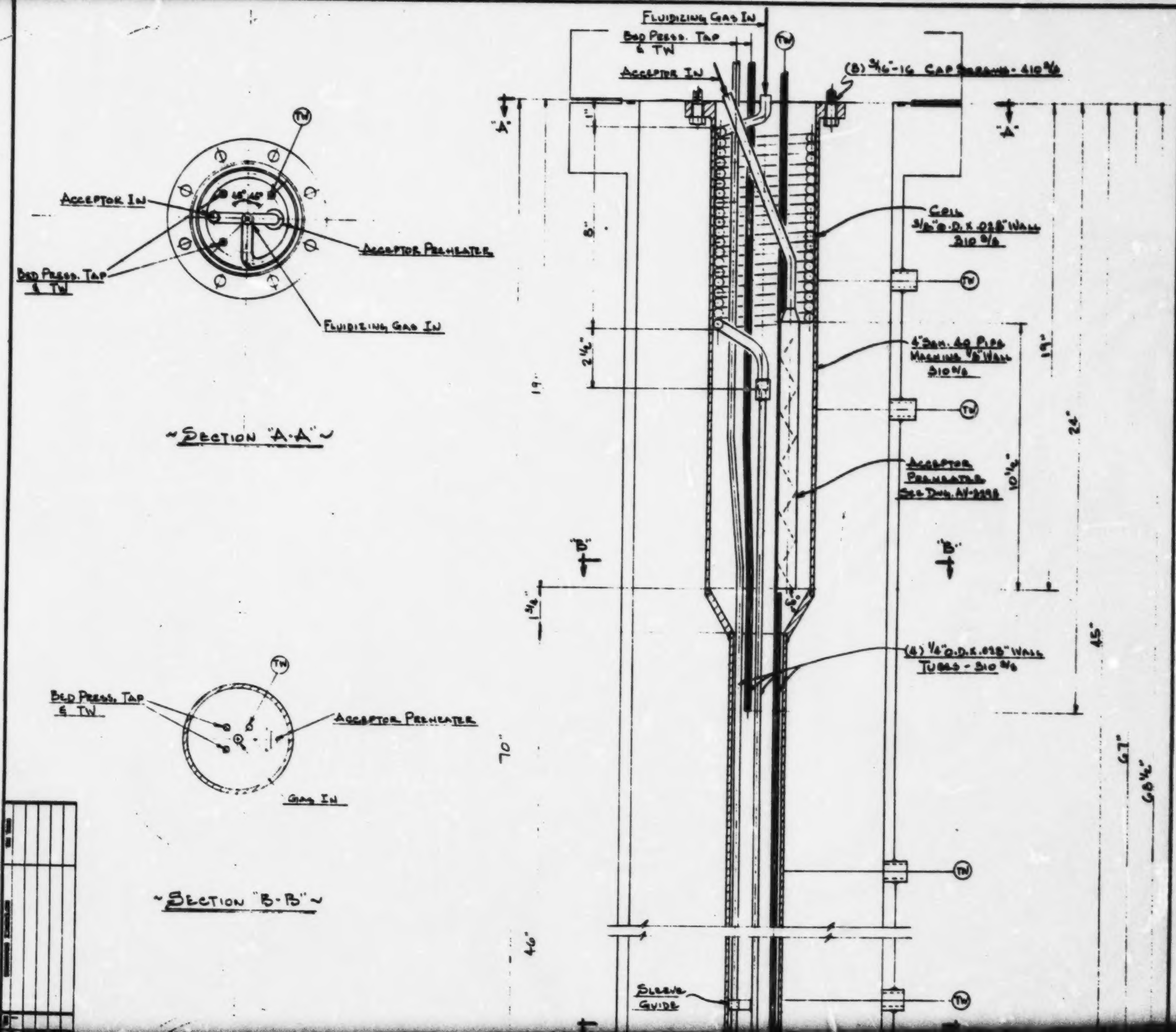
CONSOLIDATION COAL COMPANY
RESEARCH DIVISION
LIBRARY, PENNA.

D-2 GAS DESULFURIZER ASSEMBLY
LOW SULFUR BOILER FUEL UNIT

1	5-15-73	REVISED METALS - CON & TW's	
DATE	6-13-72	DR	W.A.S.

SCALE	PROJECT NO	DRAWING NUMBER	REV
1/2":1"	33300	AV-3306	1

B


Fluidizing Gas In
Bed Press. Tap & TW
Acceptor In
TW
(8) 3/8"-16 Cap Screws - 410 S/S
"A"
"A"
1"
8"
2¼"
19"
Coil 3/8" O.D. x .028" Wall 310 S/S
TW
4" Sch. 40 Pipe Machine 1/8" Wall 310 S/S
TW
19"
24"
10⅛"
Acceptor Preheater See Dwg. AY-2298
"B"
"B"
1⅛"
6"
(4) 1/4" O.D. x .028" Wall Tubes - 310 S/S
45"
70"
67"
68½"
46"
TW
TW
Sleeve Guide
Acceptor In
TW
Acceptor Preheater
Bed Press. Tap & TW
Fluidizing Gas In
~Section "A-A"~
TW
Bed Press. Tap & TW
Acceptor Preheater
Gas In
~Section "B-B"~
9

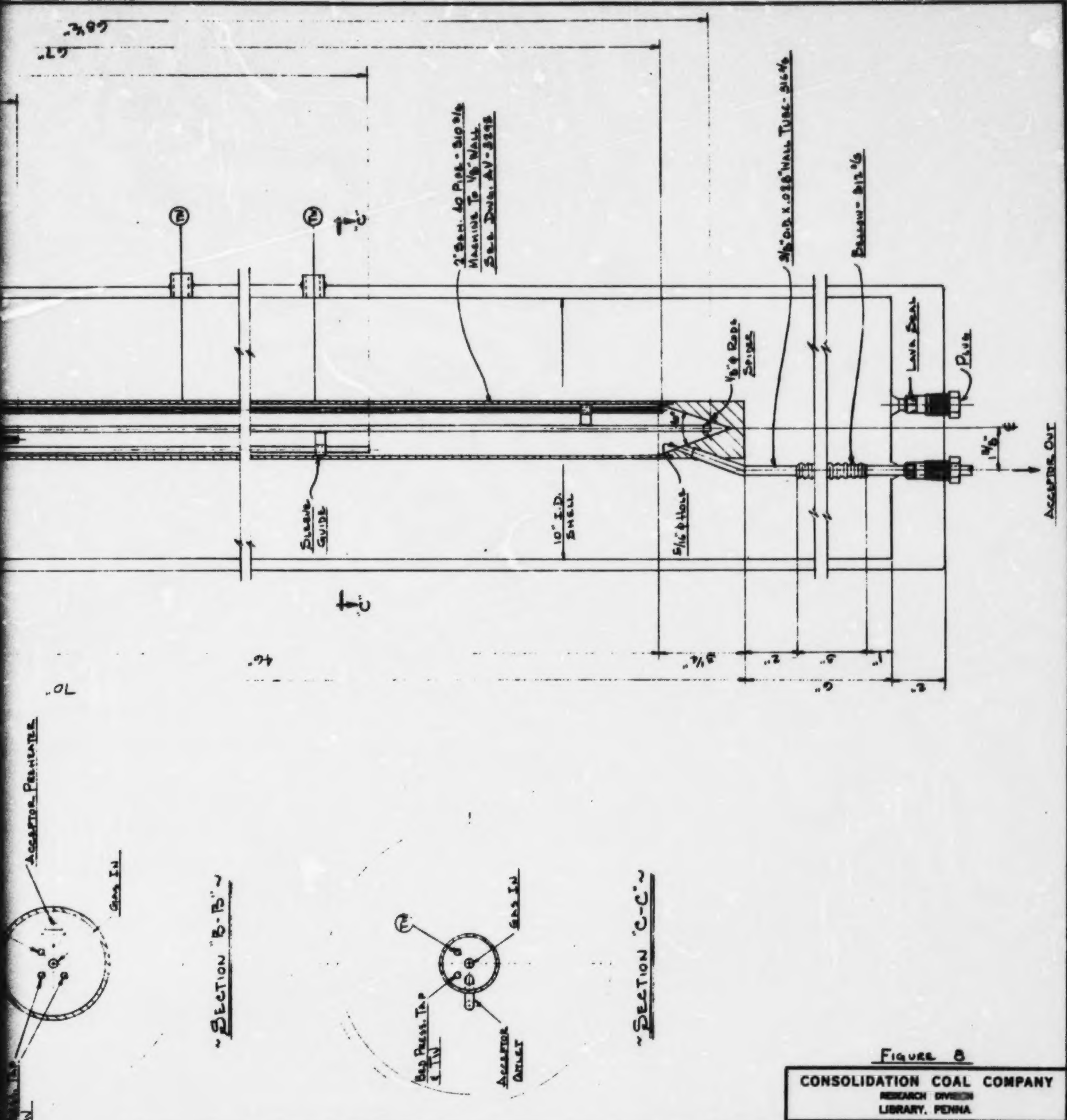

2" Sch. 40 Pipe - 310 S/S
Machine To 1/8" Wall
See Dwg. AV-3298
3/8" O.D. x .028" Wall Tube - 316 S/S
Bellow - 312 S/S
Sleeve Guide
10" I.D. Shell
1/8" ϕ Rods Spider
5/16" ϕ Hole
Lava Seal
Plug
Acceptor Out
3/8"
2
2
C
C
Section "B-B"
Section "C-C"
Acceptor Preheater
Gas In
Gas In
Bed Press. Tap & TW
Acceptor Outlet
E
D

FIGURE 8

CONSOLIDATION COAL COMPANY
RESEARCH DIVISION
LIBRARY, PENNA.

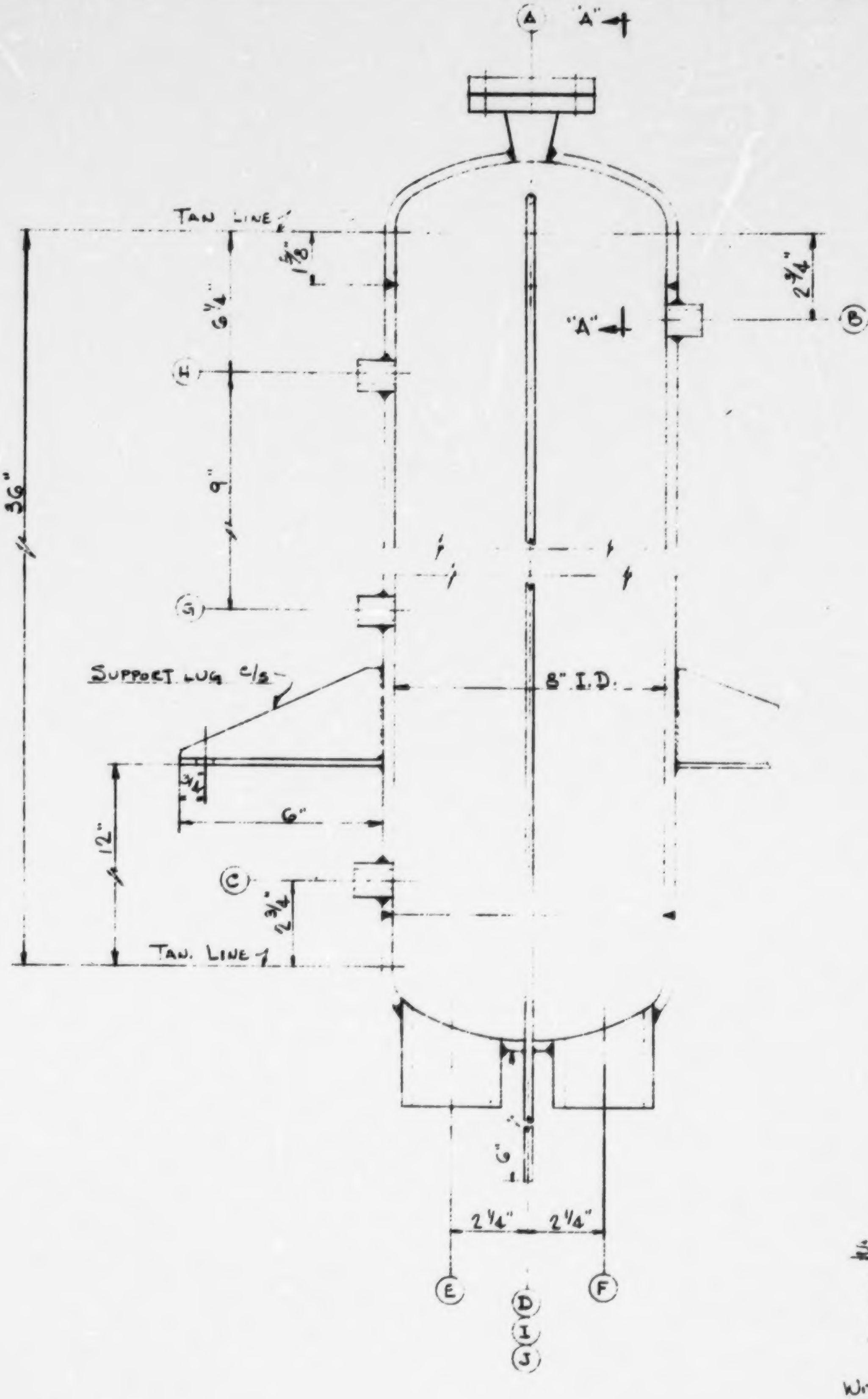
D-1 Regenerator Assembly
Low Sulfur Boiler Fuel Unit

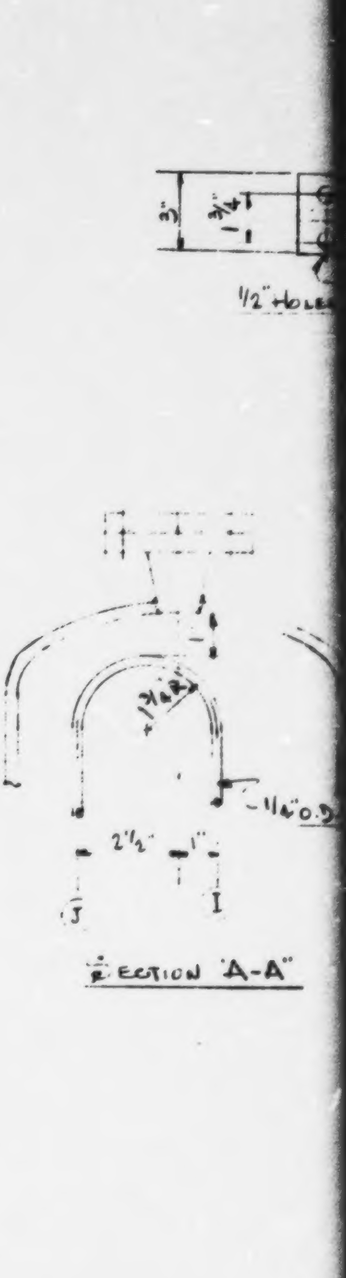
SCALE	PROJECT NO.	DRAWING NUMBER	REV.
1/2"=1"	55'2.00	AV-3294	1

DATE	5-1-72
DRN.	W.A.S.
CHK.	
APP.	
ISSUED FOR CONST.	

DWG. NO.	REFERENCE DRAWINGS	NO.	DATE	REVISION	BY	CHK.	APP.
		1	5-19-72	Revised Title			

B


A
"A"
TAN LINE
1 3/8"
2 1/4"
6 1/4"
"A"
B
H
9"
36"
G
SUPPORT LUG C/S
8" I.D.
6"
3/4"
12"
C
2 3/4"
TAN. LINE
6"
2 1/4"
2 1/4"
E
D
I
J
F


3"
1 3/4"
1/2" HOLE
1 1/4" R
1 1/4" O.D.
2 1/2"
1"
J
I

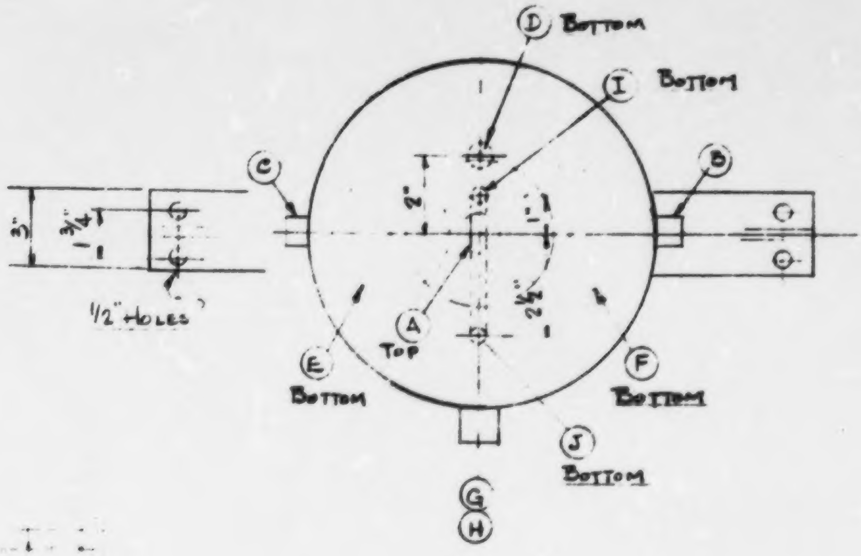
SECTION "A-A"

SPECIFICATIONS:

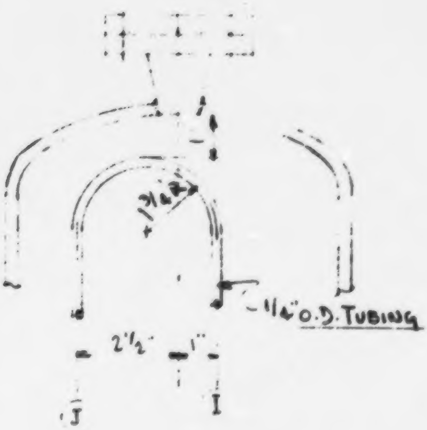
DESIGN PRESSURE = 450 PSIG
DESIGN TEMPERATURE = 400 °F
MATERIAL: 304 S/S EXCEPT A

MANUFACTURED & STAMPED
WITH ASME PRESSURE VESSEL COD
PENNA. CODE STAMP REQUIRE

A


D BOTTOM
I BOTTOM
C
B
3"
1 3/4"
1/2" HOLES
2"
1"
2 1/2"
A TOP
E BOTTOM
F BOTTOM
J BOTTOM
G
H

~ORIENTATION~


1 3/4 R
1/4" O.D. TUBING
2 1/2"
1"
J
I

SECTION "A-A"

NOZZLE SCHEDULE		
ITEM	DESCRIPTION	SERVICE
A	1/2" - 300# W.N. FLG. RF. & BLND	GAS INLET
B	1/4" COUPLING	GAS OUTLET
C	1/4" COUPLING	WATER INLET
D	1/4" COUPLING	DRAIN
E	2" COUPLING	HEATER
F	2" COUPLING	HEATER
G	1/2" HALF CPLG.	GAGE GLASS
H	1/2" HALF CPLG.	GAGE GLASS
I	1/4" O.D. TUBE	THERMOWELL
J	1/4" O.D. TUBE	THERMOWELL

FIGURE 9

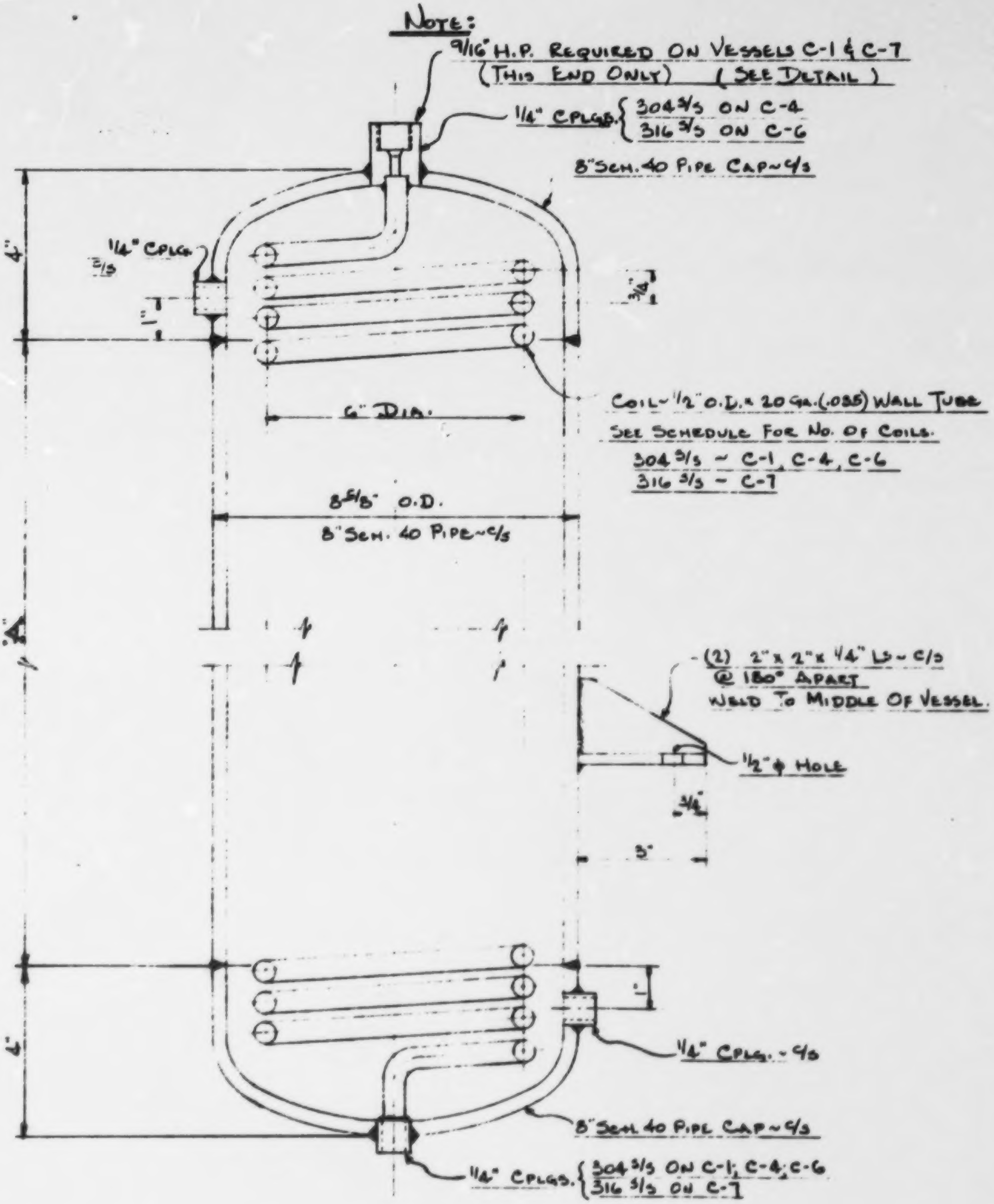
SPECIFICATIONS:

DESIGN PRESSURE = 450 PSIG
DESIGN TEMPERATURE = 400 °F
MATERIAL: 304 S/S EXCEPT AS NOTED

MANUFACTURED & STAMPED IN ACCORDANCE WITH ASME PRESSURE VESSEL CODE SECT. VIII
PENNA. CODE STAMP REQUIRED

REVISIONS	CONSOLIDATION COAL CO. RESEARCH DIVISION LIBRARY, PENNA.		
	B-1 & B-2 SATURATOR CONTINUOUS UNIT		
DRAWN WAS 1/11/71 CHKD APPD	SCALE 3/8" = 1"	PROJECT 551.00	DRAWING NO BV-3136

B



NOTE:
9/16" H.P. REQUIRED ON VESSELS C-1 & C-7
(THIS END ONLY) (SEE DETAIL)

1/4" CPLGS. {304 S/S ON C-4
316 S/S ON C-6

8" SCH. 40 PIPE CAP ~ C/S

1/4" CPLG. S/S

COIL ~ 1/2" O.D. x 20 GA. (.035) WALL TUBE
SEE SCHEDULE FOR NO. OF COILS.
304 S/S ~ C-1, C-4, C-6
316 S/S ~ C-7

8 5/8" O.D.
8" SCH. 40 PIPE ~ C/S

(2) 2" x 2" x 1/4" LS ~ C/S
@ 180° APART
WELD TO MIDDLE OF VESSEL.

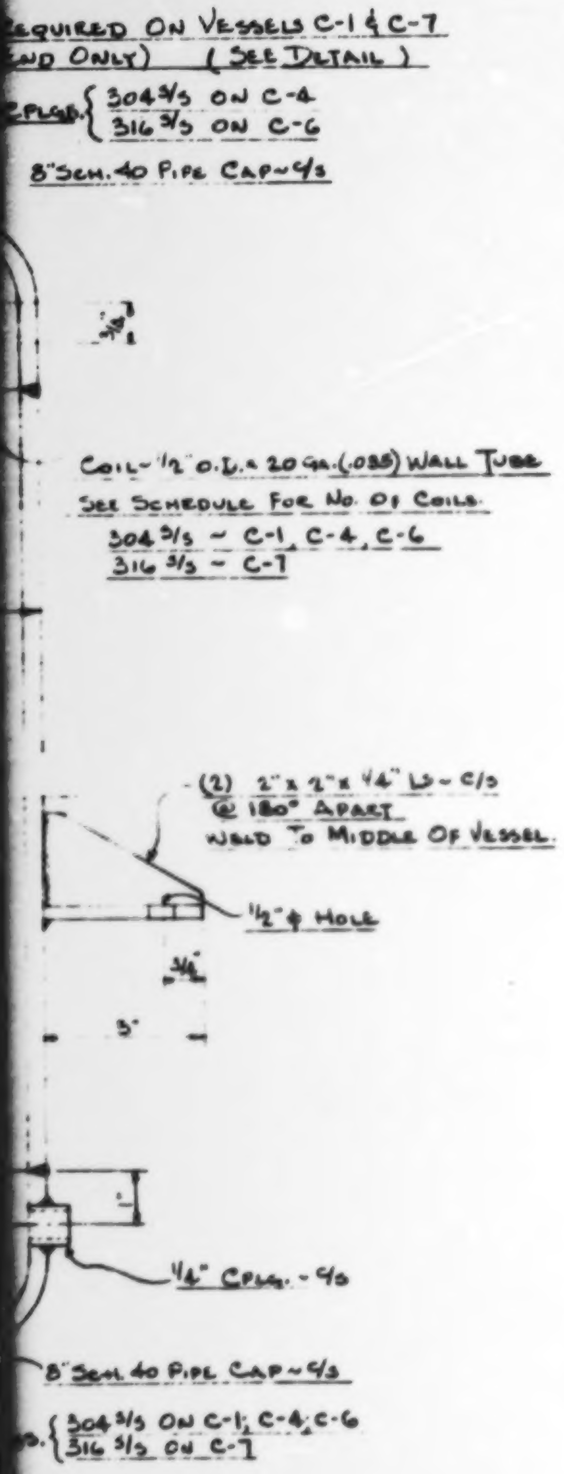
1/2" φ HOLE

1/4" CPLG. ~ C/S

8" SCH. 40 PIPE CAP ~ C/S

1/4" CPLGS. {304 S/S ON C-1, C-4, C-6
316 S/S ON C-7

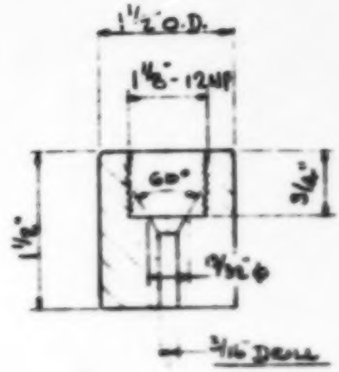
A



EQUIRED ON VESSELS C-1 & C-7
END ONLY) (SEE DETAIL)
CPLGS. { 304 S/S ON C-4
316 S/S ON C-6
8" SCH. 40 PIPE CAP ~ C/S
COIL ~ 1/2" O.D. x 20 GA. (.035) WALL TUBE
SEE SCHEDULE FOR NO. OF COILS.
304 S/S ~ C-1, C-4, C-6
316 S/S ~ C-7
(2) 2" x 2" x 1/4" LS ~ C/S
@ 180° APART
WELD TO MIDDLE OF VESSEL.
1/2" ϕ HOLE
3/4"
3"
1/4" CPLG. - C/S
8" SCH. 40 PIPE CAP ~ C/S
{ 304 S/S ON C-1, C-4, C-6
316 S/S ON C-7

~ COIL SCHEDULE ~

VESSEL No.	DIMENSION "A"	No. COILS	APPROX. FT. OF 1/2" TUBE REQ'D.
C-1	20"	32	50'
C-4	3"	9	14'
C-6	8"	16	25'
C-7	20"	32	50'



1 1/2" O.D.
1 1/8" - 12NF
60°
3/4"
1 1/2"
9/32" ϕ
3/16" DRILL

DETAIL FOR 9/16" H.P.

MAT'L: 304 S/S - C-1
316 S/S - C-7

- DESIGN CONDITIONS ~

VESSEL	PSIG	TEMP.	HYDRO TEST
C-1	450	600°F	675 PSIG
C-4	450	100°F	675 PSIG
C-6	450	800°F	850 PSIG
C-7	450	800°F	850 PSIG

FIGURE 10

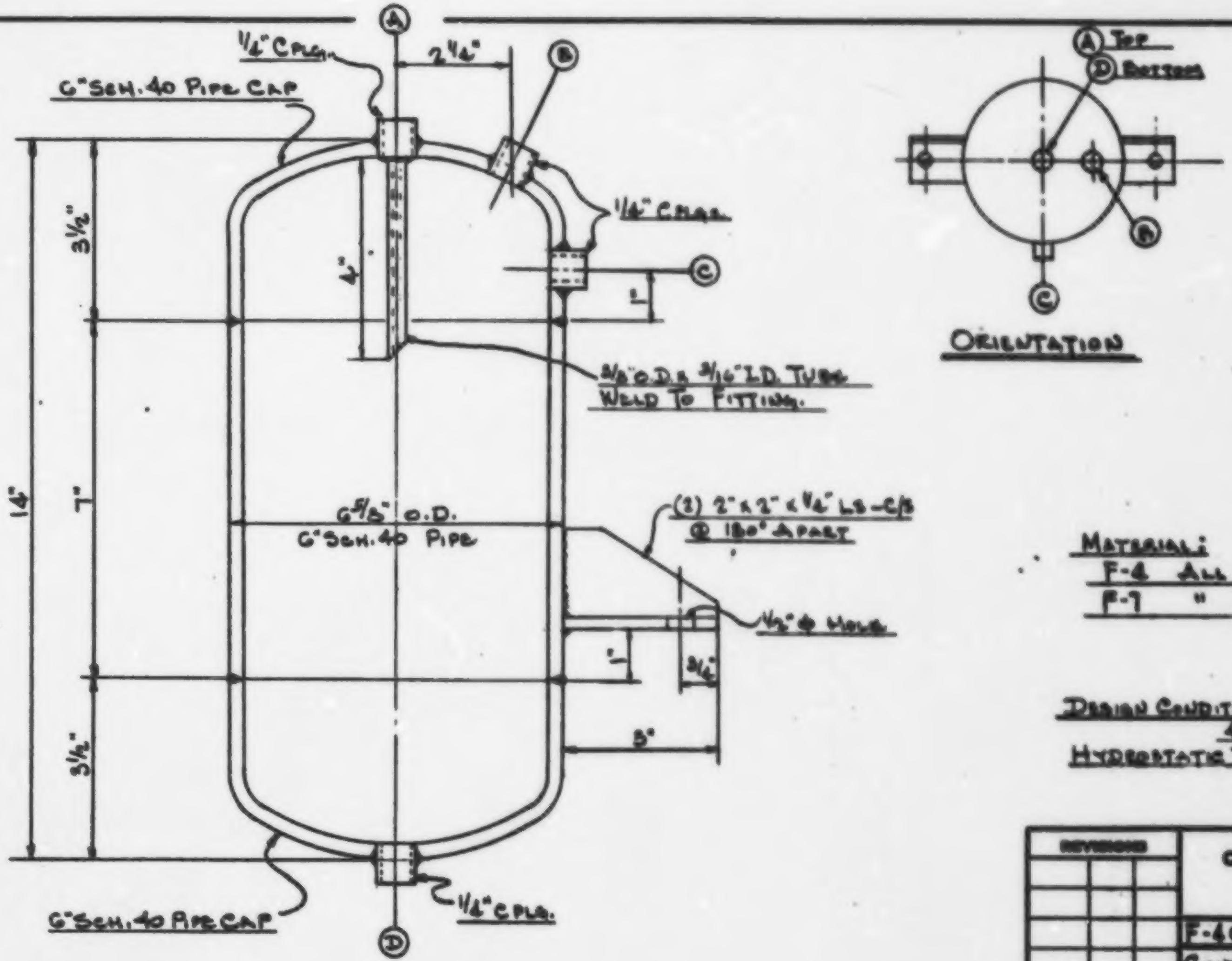
REVISIONS

CONSOLIDATION COAL CO.
RESEARCH DIVISION
LIBRARY, PENNA.

C-1, C-4, C-6, C-7 COOLERS
CONTINUOUS GASIFICATION UNIT

DRAWN 5/30/73
CHKD
APPD
SCALE 1/2" = 1"
PROJ. 552.00
DRAWING NO. BV-3426

B


Ⓐ
1/4" Cplg.
2 1/4"
Ⓑ
6" Sch. 40 Pipe Cap
1/4" Cplg.
Ⓒ
1"
4"
3 1/2"
3/8" O.D. x 3/16" I.D. Tube
Weld to Fitting.
14"
7"
6 5/8" O.D.
6" Sch. 40 Pipe
(2) 2" x 2" x 1/4" Ls - C/S
@ 180° Apart
1/2" ⌀ Hole
1"
3/4"
3"
3 1/2"
6" Sch. 40 Pipe Cap
1/4" Cplg.
Ⓓ
Ⓐ Top
Ⓓ Bottom
Ⓑ
Ⓒ
Orientation

Material:
F-4 All 304 S/S Except Mounting Legs
F-7 " 316 S/S " " "

Design Conditions:
480 Psig @ 100°F
Hydrostatic Test: 675 Psig

Figure 11

CONSOLIDATION COAL CO.
RESEARCH DIVISION
LIBRARY, PENNA.
F-4 & F-7 Condensate Receivers
Continuous Gasification Unit
5/30/72
Scale 3/8" = 1"
352.00
CV-3425
REV.

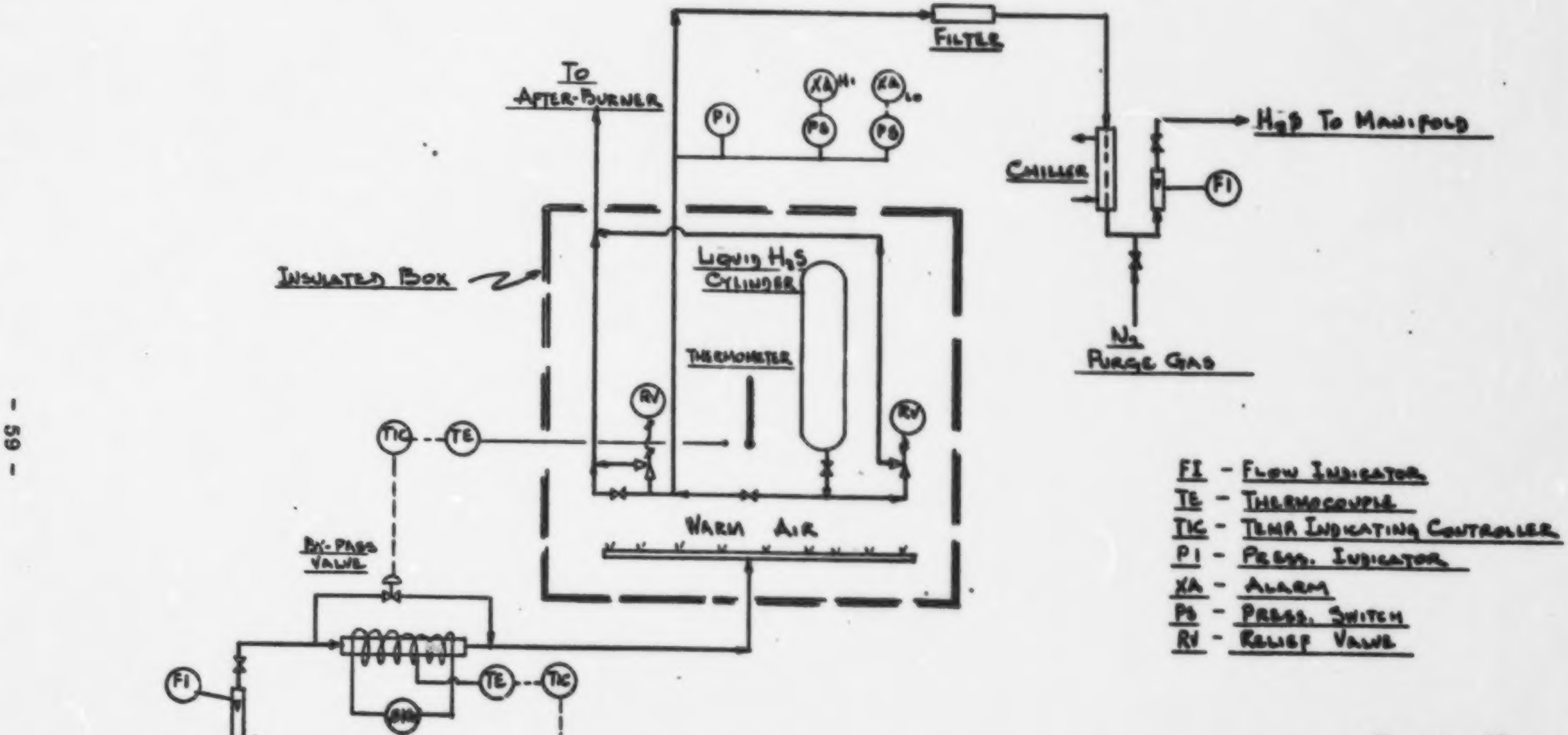

To After-Burner
Filter
H$_2$S To Manifold
Chiller
FI
N$_2$ Purge Gas
XA Hi
XA Lo
PI
PS
PS
Insulated Box
Liquid H$_2$S Cylinder
Thermometer
RV
RV
TIC
TE
Warm Air
By-Pass Valve
FI
TE
TIC
Air
FI - Flow Indicator
TE - Thermocouple
TIC - Temp. Indicating Controller
PI - Press. Indicator
XA - Alarm
PS - Press. Switch
RV - Relief Valve

Figure 12

REVISIONS

CONSOLIDATION COAL CO.
RESEARCH & DEVELOPMENT DIVISION
LIBRARY, PENNA.

Flow Diagram
H$_2$S Supply System

DRAWN 5/21-73
CHKD.
APPD.
SCALE None
PROJECT 552.00
DRAWING NO. CF-3421

B. Operating Procedure for a Typical Two-Vessel Integrated Run

1. Prerun Procedure

The acceptor inventory was made up to the desired size consist. About 11,000 grams of raw acceptor was used in a typical run.

After bringing the gas desulfurizer and regenerator to the programmed temperatures, the unit was pressured up with nitrogen to 15 atmospheres and was leak tested.

2. Startup

With the unit at pressure, the recycle compressor was started and, after setting the desired compressor discharge pressure, the programmed recycle flows to the gas desulfurizer were established.

The programmed flows of CO_2, N_2, and H_2, were then put into the appropriate vessels. The steam flow was established by diverting the fluidizing gas through the steam generator. The Powerstats on the steam generator heater were adjusted to control the programmed water temperature.

The acceptor feed hoppers were charged and feeding was begun at the programmed rate. At this time the feeder was fine tuned to give the desired feed rate by checking the time required to empty a hopper with a known weight of acceptor.

The emergency solenoid valve which isolated the process vessels was kept closed until the acceptor filled the L-5 standleg and the gas desulfurizer vessel.

The entire acceptor inventory was circulated through the unit in order to calcine the $MgCO_3$ component of the dolomite and to adjust the level controllers.

As the acceptor was circulated, the L-5 valve positions corresponding to normal and low acceptor levels in the gas desulfurizer, and the L-6 valve setting corresponding to high, normal and low levels in the regenerator were adjusted until the optimum settings were obtained.

When an acceptor feed hopper became empty, the parallel hopper was switched on-stream. Simultaneously, the acceptor withdrawal hoppers were switched. The off-stream withdrawal hopper was isolated and emptied. After all of the raw acceptor had been fed to the unit, the acceptor which had been removed from withdrawal hoppers was combined. Two batches of the combined acceptor weighing about 2100 grams each were made up and charged one batch to each feed hopper. These two batches constituted the initial external acceptor inventory for the run.

When all of the raw acceptor had been fed, the L-4 feeder was shut off. The gas desulfurizer bed was presulfided by feeding H_2S at the programmed rate long enough to sulfide 20% of the useful calcium content of the acceptor in the bed. Acceptor circulation was then restarted, and this marked the beginning of the run.

When acceptor circulation was restarted, the Powerstats controlling the electrical heat input to both vessels were adjusted to give the desired bed temperature. Axial temperature traverses were taken across both fluidized beds and the electrical heat inputs to the heating zones were further adjusted to give a flat temperature profile.

3. Routine Run Procedure

Continuous acceptor circulation was maintained by feeding acceptor to the gas desulfurizer alternately from the two acceptor feed hoppers. The acceptor feed hoppers and regenerator withdrawal hoppers were switched simultaneously. The off-stream withdrawal hopper was isolated from the unit and drained. The acceptor removed from the withdrawal hoppers was charged to the off-stream acceptor feed hopper. Riffled 20-gram samples were taken at specified times during the run.

Samples were also periodically removed from the L-5 line during the run.

The concentrations of CO and CO_2 in the gas desulfurizer offgas were monitored on infrared analyzers. CO_2 in the regenerator offgas was followed on the thermal conductivity cell. During the course of the run, several samples from each reactor were analyzed on the gas chromatograph. Iodine scrubbers were used to check the level of H_2S in the offgas from both reactors. During some runs, the exit gases were sampled [illegible] a high pressure cylinder and sent to the analytical laboratory for exhaustive chromatographic analysis.

The flasks which were used to collect the condensate drained from the condensate receivers were replaced hourly, and the weight of the condensate determined. The condensates collected in the sight glasses below the C-4 and C-6 coolers were drained and weighed at least once per shift.

The solids filters in the gas desulfurizer and regenerator outlet gas piping were changed when the ΔP across the on-stream filter was 75" H_2O. After the filters were switched, the off-stream filter was removed from the unit, cleaned, and reinstalled. The contents of each filter were weighed and saved for analysis.

The rotameter settings and product gas meter readings were recorded hourly as were the important pressures, pressure drops, temperatures and Powerstat settings.

4. Shutdown Procedures

At shutdown, the run was ended by simultaneously shutting off the H_2S flow to the gas desulfurizer, shutting off the acceptor feeder, L-4, and closing the emergency solenoid valve between the vessels.

The steam and H_2 flows were removed from both vessels as soon as possible after the end of the run. Immediately thereafter, the contents of the regenerator were withdrawn. The E-2 emergency valve was then reopened and the gas desulfurizer bed was withdrawn through the regenerator. The recycle compressor was then shut down and the unit was depressurized and allowed to cool.

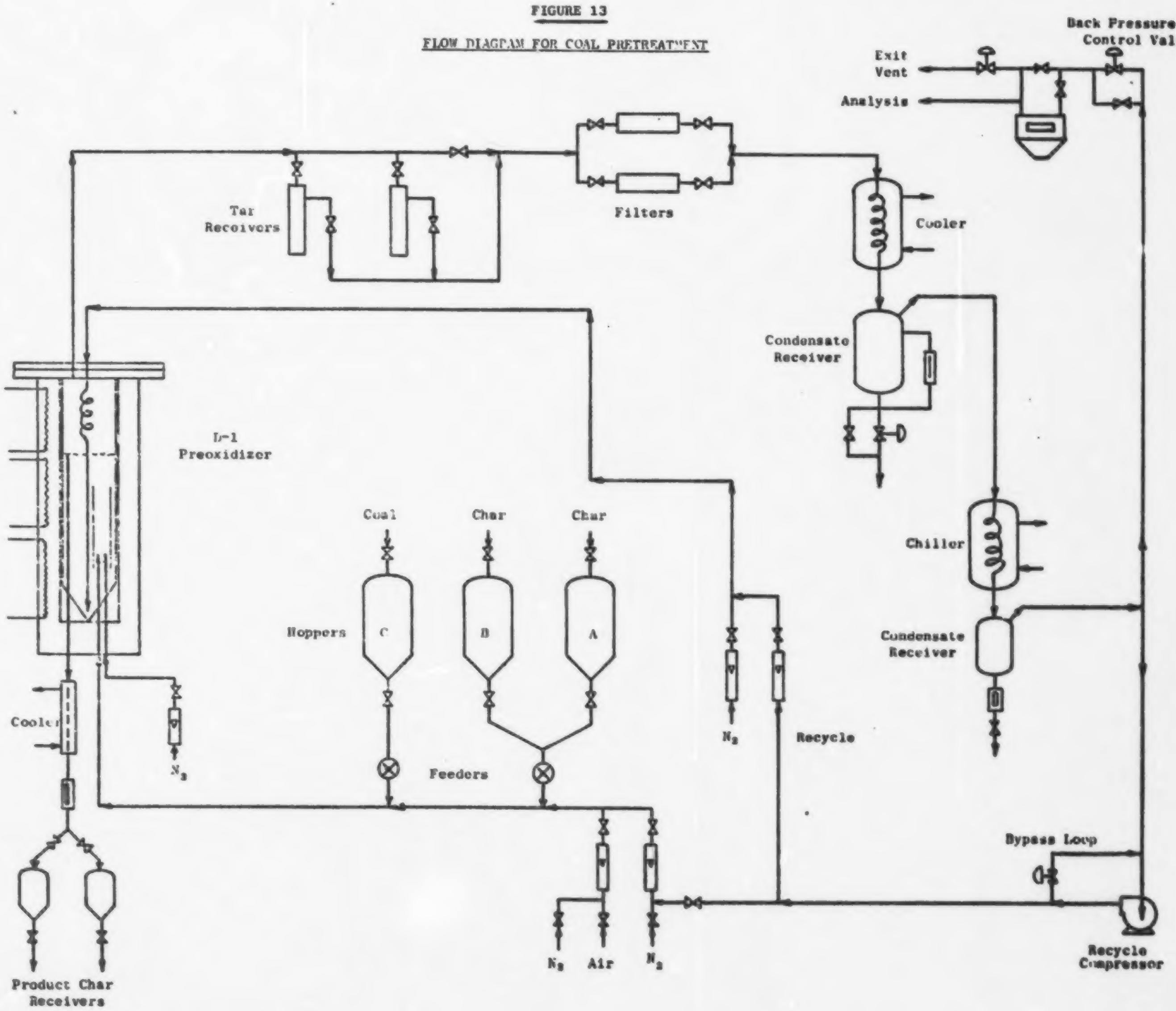
C. Equipment and Procedure for Single-Vessel Operation

1. Pretreatment Operations

Only the reactor vessel, D-1, was used in the pretreatment studies. A simplified flow diagram for this system is shown in Figure 13. The system was used for both the Seeded Coal Process tests and for preoxidation runs. A bed of noncaking char was fed to the reactor for start-up in both cases.

FIGURE 13

FLOW DIAGRAM FOR COAL PRETREATMENT


Back Pressure Control Valve
Exit Vent
Analysis
Tar Receivers
Filters
Cooler
Condensate Receiver
D-1 Preoxidizer
Chiller
Coal
Char
Char
Hoppers
C
B
A
Condensate Receiver
Cooler
N_2
Feeders
N_2
Recycle
Bypass Loop
Product Char Receivers
N_2
Air
N_2
Recycle Compressor

Two reactors were used. No. 1 shown in Figure 14 was left from the previous contract period and was equipped with a boot arrangement. This was changed to No. 2 when the draft tube Configuration C was installed. The reactor used in the acceptor sulfur cycle work is shown for comparison.

Coal and char feeds were put in through one outlet line, and product was withdrawn through the other outlet line. An overflow weir was used to maintain the bed level. Tar receivers were connected to the system, and all of the analyzers were connected to the pretreater vessel. This included the infrared SO_2 analyzer and the paramagnetic oxygen analyzer which were not used for the acceptor studies.

Figures 15 and 16 detail the draft tube arrangements which were tied in the Seeded Coal Process experiments. The reasons for choosing these particular designs are elaborated upon in the Pretreatment Section of this report (Section VIII).

Pretreater outlet gas generally contained some heavy tar and pitch which would rapidly plug the solids filters and the outlet piping. This was alleviated by installing two parallel tar receivers or knock-out pots to collect the heavy material as shown in Figure 13. The upstream piping was heated to prevent condensation of tar and pitch. The tar receivers were water cooled to ensure condensation of heavy tars; some water also inevitably was condensed.

To begin preoxidation, the bed was brought to temperature with only nitrogen being fed. The coal feed and air were both begun at a reduced rate. The nitrogen flow was diminished in accordance with the increasing air feed. At the same time the electrical heat input was reduced and the temperature was stabilized at the programmed level. Since only a fraction of the final air was being fed, severe temperature excursions were avoided. The final feed rates of coal and air were approached in several steps.

The run was shut down by first turning off the coal feed. The air flow was kept at half rate for 15 minutes while the bed was cooling. This was to prevent possible agglomeration from occurring in the hot bed in the absence of air. Air was then shut off and the bed was drained under nitrogen.

To begin a Seeded Coal Process test, the bed was first brought to temperature in nitrogen. Shortly before the coal was to be fed, the programmed air flow was begun and the Powerstats were cut back to compensate for the oxidative heat release. Seed char was then fed followed by the fine Ireland Mine coal.

The run was stopped by simultaneously shutting off the coal and air feeds.

2. Demonstration Runs

For the demonstration runs, the vessel, D-1, was used. A simplified flow diagram for this system is given in Figure 17. The No. 2 reactor of Figure 14 was used. Char was fed in through the acceptor outlet line, L-6, and removed via outlet line, L-2. An overflow weir was used to maintain the bed level. All of the analyzers were connected to the D-1 reaction vessel.

A bed of char was fed to the reactor which was then brought to temperature using programmed flows excepting the substitution of nitrogen for air. To begin the run, the electrical heat was cut back and air replaced a portion of the nitrogen. The run was ended by turning off the air and char feeds.

3. Gasification Kinetics Runs

A flow diagram of the system is given in Figure 18. Char was fed into the reactor through a dip tube which extended into the cone of the reactor, and was removed through an overflow weir.

The bed of start-up char was brought to temperature using the programmed flows for all gases. The exit gas analyzers were carefully watched, and the balance period was begun when gas concentrations in the offgas had reached steady state and three bed inventories were replaced. The run was shut down by diverting the gas stream out of saturator and shutting off the char feeder.

The system configuration shown in Figure 18 also was used for pretreatment of the master batch of char feed to the kinetics runs.

4. Carbon Burnup Cell Tests

For study of the carbon burnup reactor, the D-2 vessel internals were modified as shown in Figures 19 and 20. The solids and gas inlets were joined inside the reactor to form a Y so that they entered together. In order to survive the severe oxidizing atmosphere, all the internals were fabricated of 310 stainless steel.

The D-2 vessel bottom was plugged so that the only exit was overhead. The exit line was led to the D-1 vessel which was used as a large ash filter and reservoir. The exit line of the ash reservoir was equipped with two No. S-78-6F Pall Trinity Micro Corporation filters which were welded into a single long unit. The filters were 316 stainless steel with a 20 micron mean pore size.

All the gas analyzers were connected to the burnup reactor.

The run was prepared by filling the burnup reactor with an inert bed of sand or dead-burned dolomite, which was fluidized with the programmed gas flows. The run was started by reducing the electrical heat input and starting the char feeder.

Ash was collected in the D-1 vessel which was emptied after the entire run was over. The run was ended by turning off the char feeder.

D. Liquid-Phase Claus Reaction Equipment and Procedure

A schematic diagram of this apparatus is shown in Figure 21. SO_2 and H_2S were fed into the reactor in two ways. In the beginning of the program, an H_2S-CO_2 mix was used in combination with purchased laboratory grade sulfurous acid. Later, two separate gas mixes, SO_2-CO_2 and H_2S-CO_2 were fed to the column. Steam was added to the gas mixture in a saturator. Absorbent liquid was fed from pressurized feed tanks. Liquid recycle was effected by charging filtered recovered product back to the feed tanks. All flows were measured with rotameters. The column was set up for continuous cocurrent downflow operation.

The reactor was a Jerguson sight gauge with an internal cross section of 5/8" x 3/4" and was 54" long. All wetted metal parts were type 316 stainless steel. Mica covers protected the glass faceplates. The packing consisted of 3 mm glass beads.

Liquid-gas separation took place just below the reactor. A sight gauge then was used as a settler to separate the absorbent liquid from liquid sulfur.

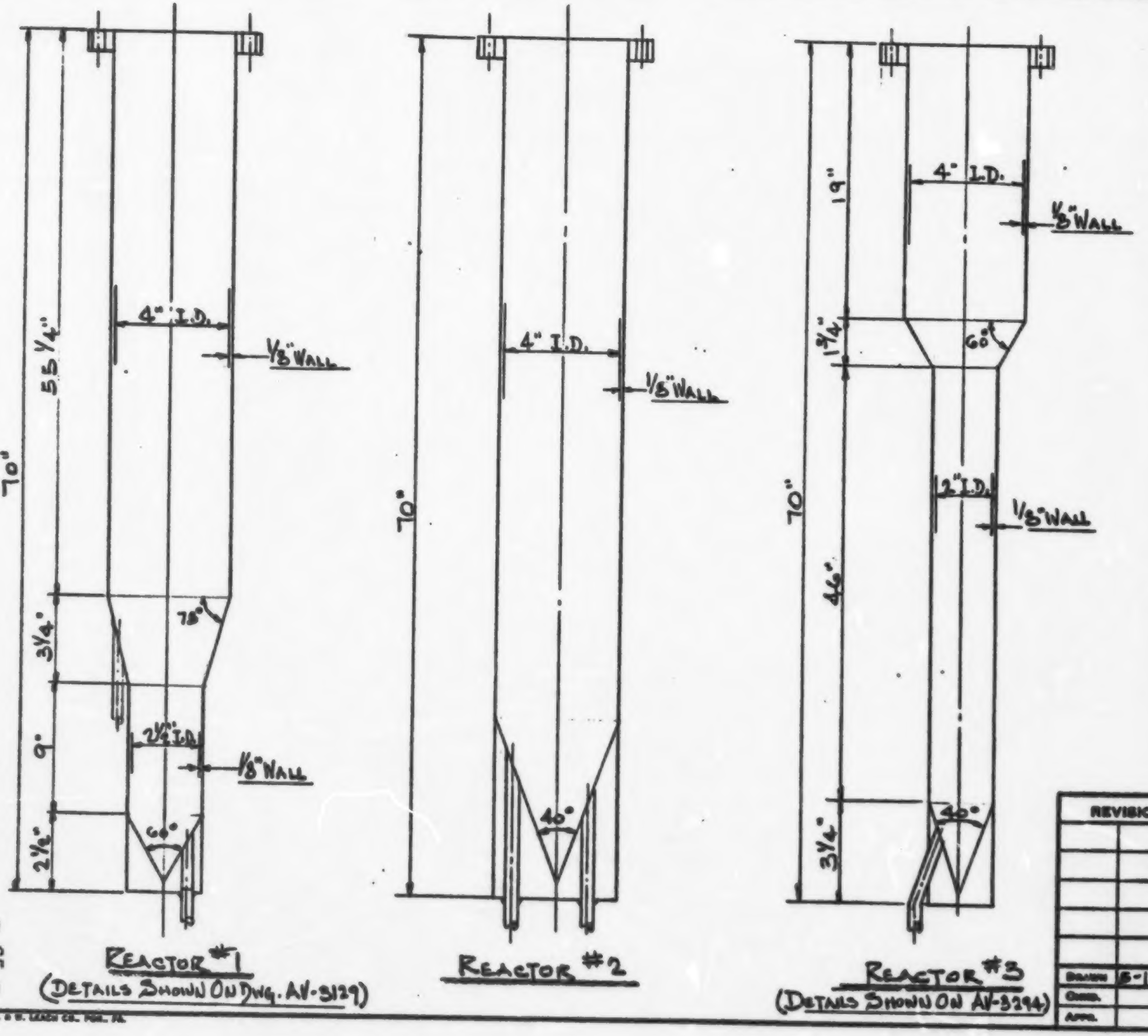

70"
55 1/4"
3 1/4"
9"
2 1/2"
4" I.D.
1/8" WALL
75°
2 1/2" I.D.
1/8" WALL
60°
REACTOR #1
(DETAILS SHOWN ON DWG. AV-3129)
70"
4" I.D.
1/8" WALL
40°
REACTOR #2
70"
19"
1 3/4"
46"
3 1/4"
4" I.D.
1/8" WALL
60°
2" I.D.
1/8" WALL
40°
REACTOR #3
(DETAILS SHOWN ON AV-3294)

FIGURE 14

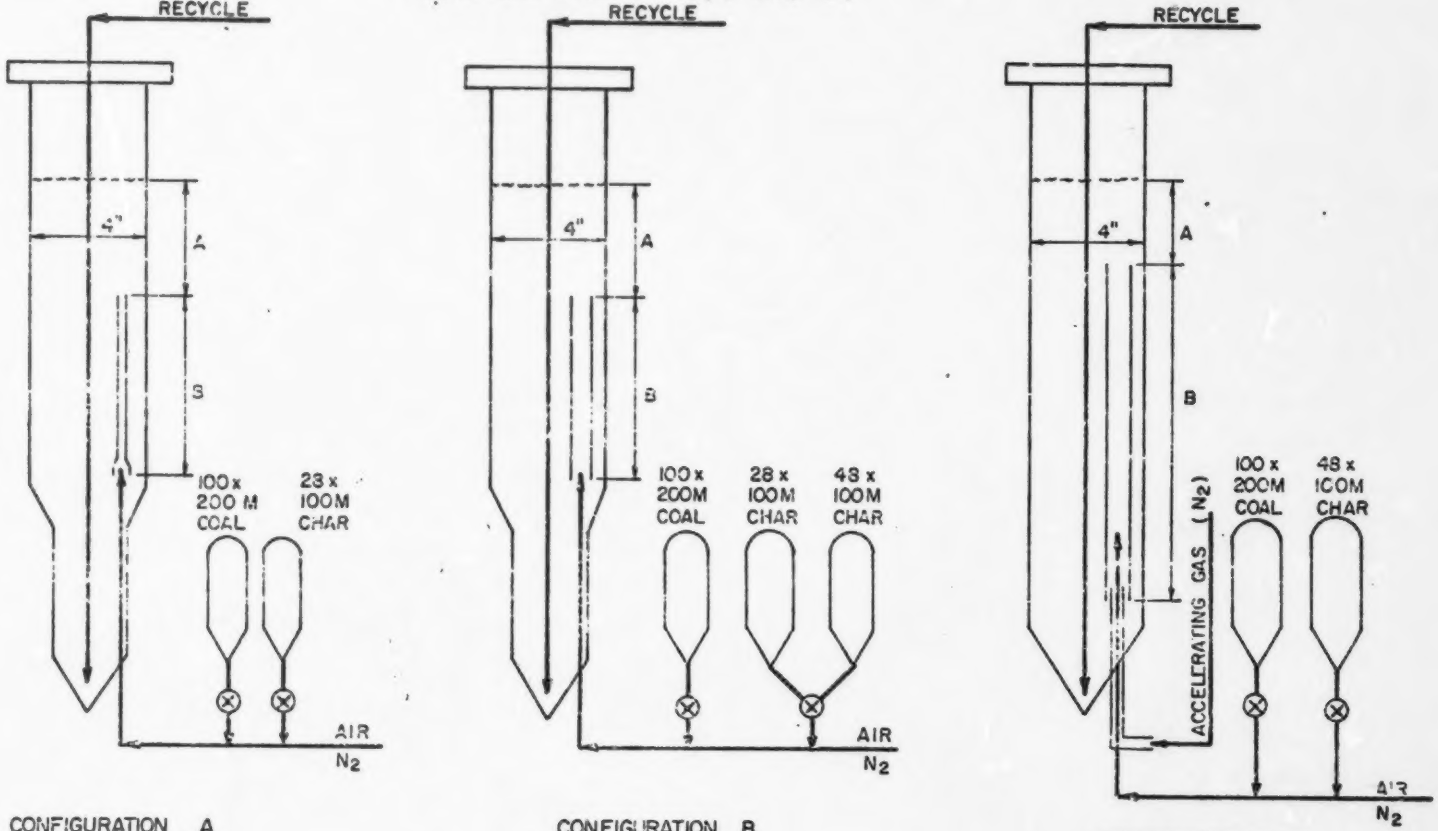
REVISIONS			CONSOLIDATION COAL CO. RESEARCH & DEVELOPMENT DIVISION LIBRARY, PENNA.		
			SCHEMATIC OUTLINE OF REACTORS FOR VESSEL D-1		
DRAWN	5-18-73		SCALE NONE	PROJECT 552.00	DRAWING NO. CV-3420
CHKD.					
APPR.					

Reproduced from best available copy.

FIGURE 15

CONFIGURATION OF DRAFT TUBES USED IN DRAFT TUBE AND SEEDED COAL TESTS

(CONFIGURATIONS A, B and C)

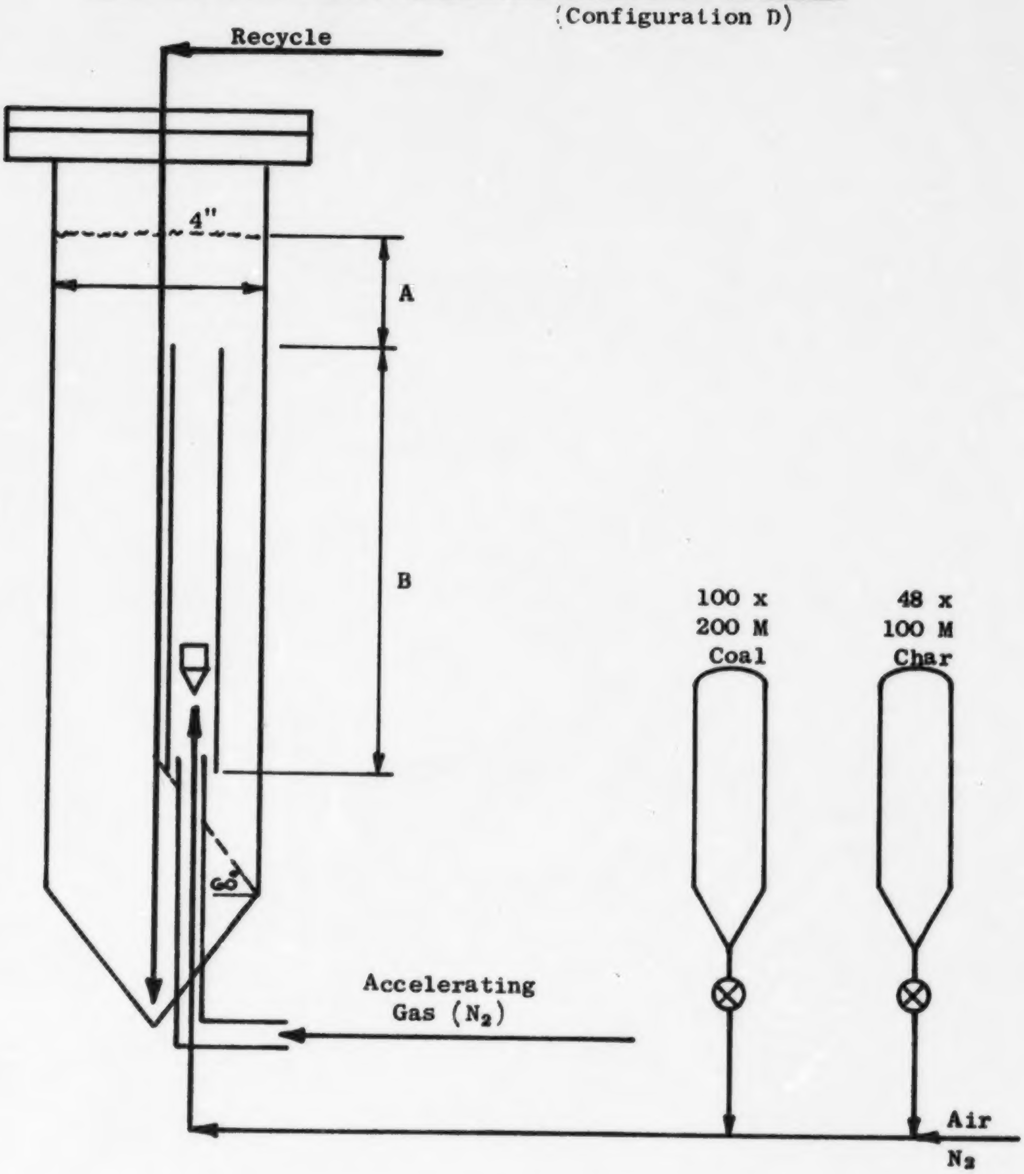

RECYCLE
4"
A
B
100x 200 M COAL
23 x 100M CHAR
AIR
N_2
RECYCLE
4"
A
B
100x 200M COAL
28 x 100M CHAR
48 x 100M CHAR
AIR
N_2
RECYCLE
4"
A
B
ACCELERATING GAS (N_2)
100 x 200M COAL
48 x 100M CHAR
AIR
N_2

	CONFIGURATION A	CONFIGURATION B	CONFIGURATION C
Dimension A	8"	8"	6"
Dimension B	24"	24"	34"
Draft Tube	.500"O.D. x .444" I.D.	.750"O.D. x .680" I.D.	.750"O.D. x .680" I.D.
Coal Feed Line	.250"O.D. x .180" I.D. tip positioned halfway into skirt	.250"O.D. x .180" I.D. tip positioned 1 inch above bottom of tube	.250"O.D. x .180" I.D. tip positioned 5 inches above bottom of tube
Accelerating Gas Line	—	—	.375"O.D. x .305" I.D. tip positioned 1 inch above bottom of tube

FIGURE 16

Configuration of Draft Tube Used in Seeded Coal Tests

(Configuration D)


Recycle
4"
A
B
60°
100 x
200 M
Coal
48 x
100 M
Char
Accelerating
Gas (N_2)
Air
N_2

CONFIGURATION D

Dimension A	4"
Dimension B	34"
Draft Tube	.750" O.D. x .680" I.D.
Coal Feed Line	.250" O.D. x .180" I.D. Tip positioned 5-inches above bottom of tube
Accelerating Gas Line	.375" O.D. x .305" I.D. Tip positioned 1-inch above bottom of tube
External Baffle	3-5/8" x 1-3/4" Elliptical, 60° from the horizontal
Internal Baffle	3/8" D x 60° Cone Tip positioned 1/2" above coal feed line

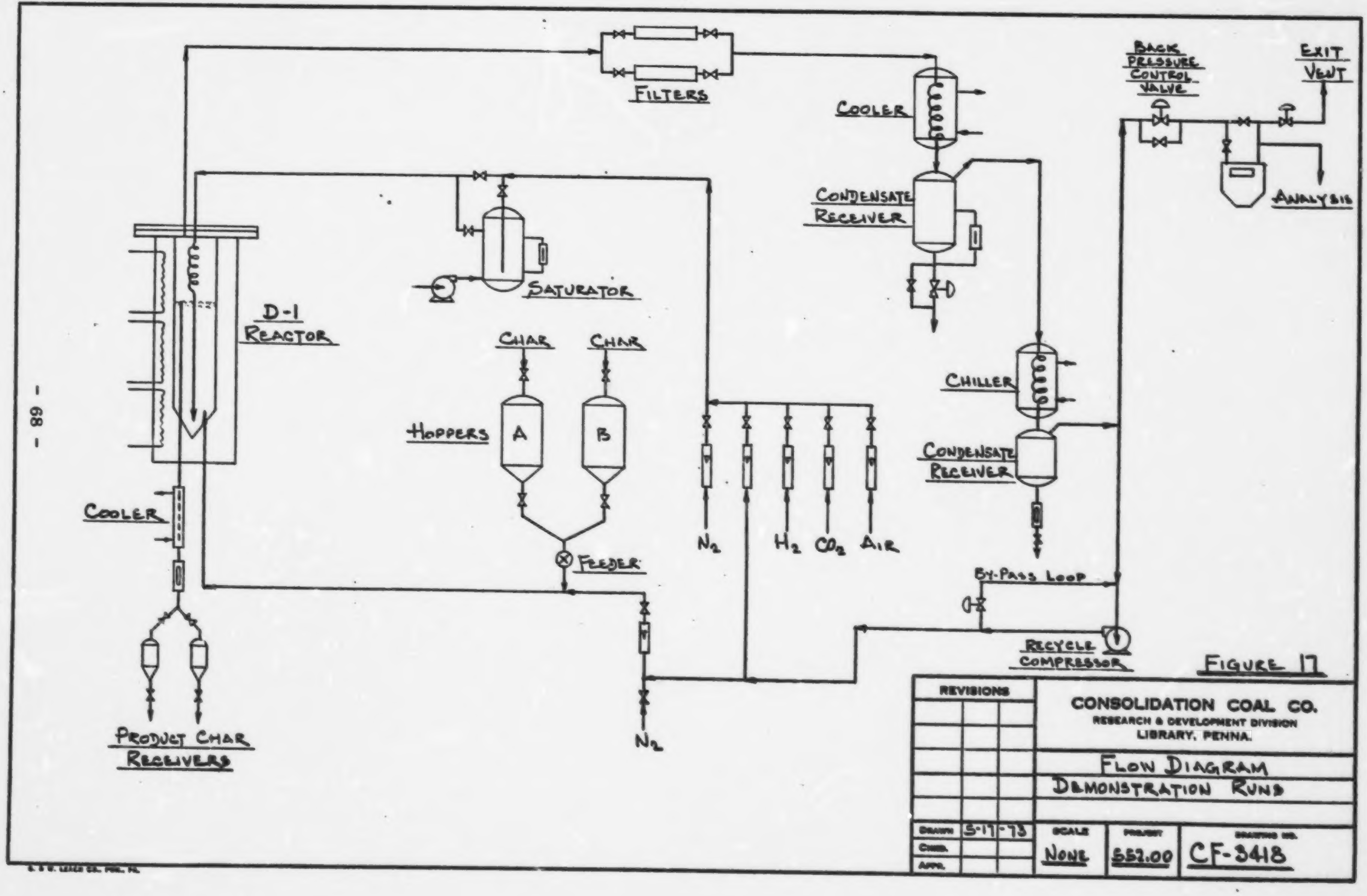

Filters
Cooler
Back Pressure Control Valve
Exit Vent
Analysis
Condensate Receiver
Saturator
D-1 Reactor
Char
Char
Hoppers
A
B
Chiller
Condensate Receiver
Cooler
N_2
H_2
CO_2
Air
Feeder
By-Pass Loop
Recycle Compressor
Product Char Receivers
N_2
REVISIONS
CONSOLIDATION COAL CO.
RESEARCH & DEVELOPMENT DIVISION
LIBRARY, PENNA.
Flow Diagram
Demonstration Runs
Drawn 5-17-73
Chkd.
Appd.
Scale None
Project 552.00
Drawing No. CF-3418

FIGURE 17

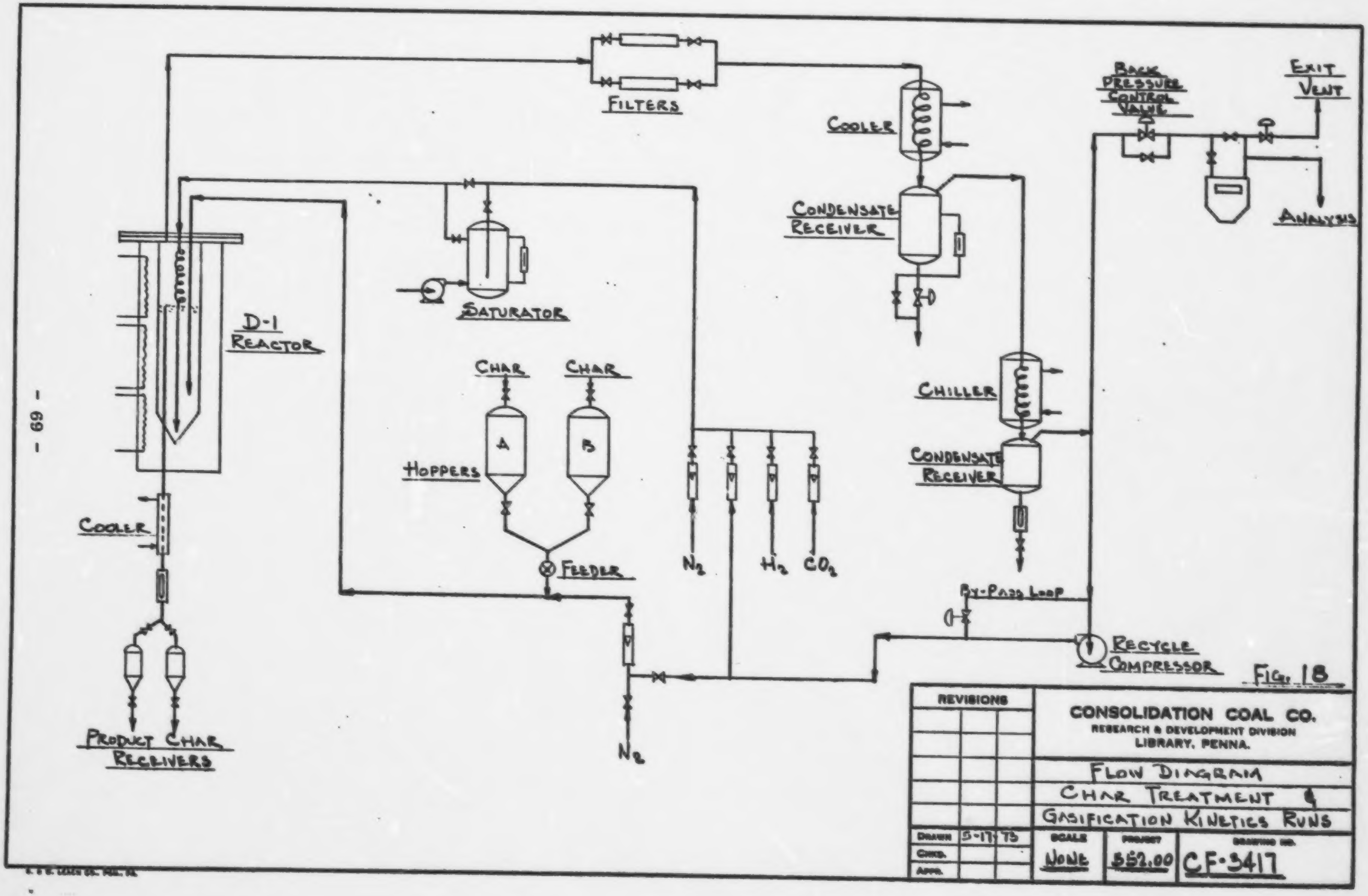

Filters
Cooler
Condensate Receiver
Back Pressure Control Valve
Exit Vent
Analysis
Saturator
D-1 Reactor
Char
Char
A
B
Hoppers
Feeder
N_2
H_2
CO_2
Chiller
Condensate Receiver
By-Pass Loop
Recycle Compressor
Cooler
Product Char Receivers
N_2
Revisions

Fig. 18

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RESEARCH & DEVELOPMENT DIVISION
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FLOW DIAGRAM
CHAR TREATMENT &
GASIFICATION KINETICS RUNS

DRAWN	5-17-75	SCALE	PROJECT	DRAWING NO.	
CHKD.		NONE	552.00	CF-3417	
APPD.					

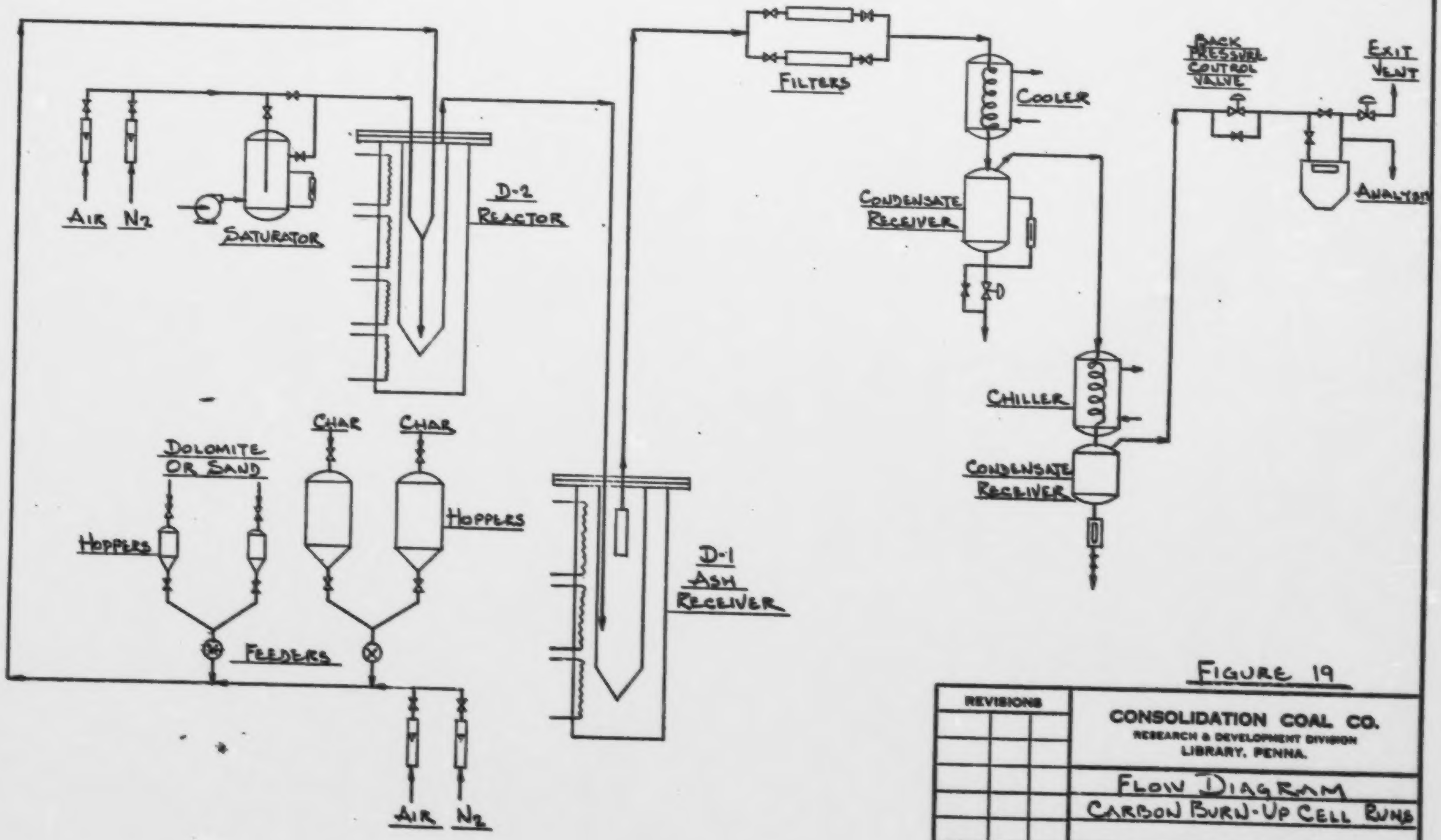
AIR
N2
SATURATOR
D-2
REACTOR
FILTERS
COOLER
CONDENSATE
RECEIVER
BACK
PRESSURE
CONTROL
VALVE
EXIT
VENT
ANALYSIS
CHILLER
CONDENSATE
RECEIVER
DOLOMITE
OR SAND
CHAR
CHAR
HOPPERS
HOPPERS
D-1
ASH
RECEIVER
FEEDERS
AIR
N2

FIGURE 19

REVISIONS		

CONSOLIDATION COAL CO.
RESEARCH & DEVELOPMENT DIVISION
LIBRARY, PENNA.

FLOW DIAGRAM
CARBON BURN-UP CELL RUNS

DRAWN	5-16-73	SCALE	PROJECT	DRAWING NO.
CHKD.		NONE	552.00	CF-3416
APPD.				

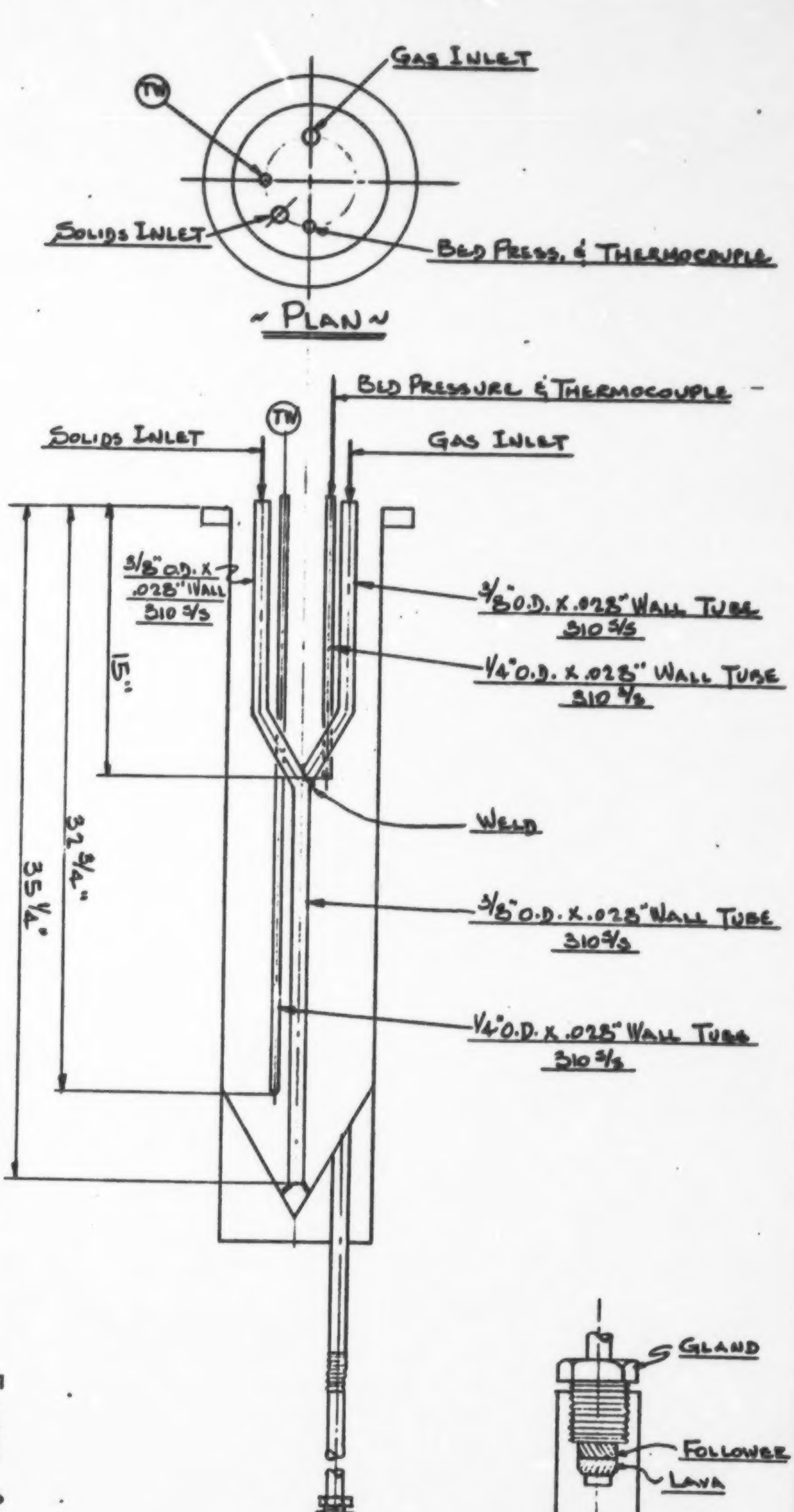
TW
GAS INLET
SOLIDS INLET
BED PRESS. & THERMOCOUPLE
~ PLAN ~
BED PRESSURE & THERMOCOUPLE
TW
SOLIDS INLET
GAS INLET
3/8" O.D. X .028" WALL 310 S/S
3/8" O.D. X .028" WALL TUBE 310 S/S
1/4" O.D. X .028" WALL TUBE 310 S/S
15"
32 3/4"
35 1/4"
WELD
3/8" O.D. X .028" WALL TUBE 310 S/S
1/4" O.D. X .028" WALL TUBE 310 S/S
PLUG
GLAND
FOLLOWER
LAVA
~ PLUG ~

FIGURE 20

REVISIONS

DRAWN 5-18-73
CHKD.
APPD.

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RESEARCH & DEVELOPMENT DIVISION
LIBRARY, PENNA.

CARBON BURN-UP CELL
REACTOR

SCALE NONE
PROJECT 552.00
DRAWING NO. CV-3419

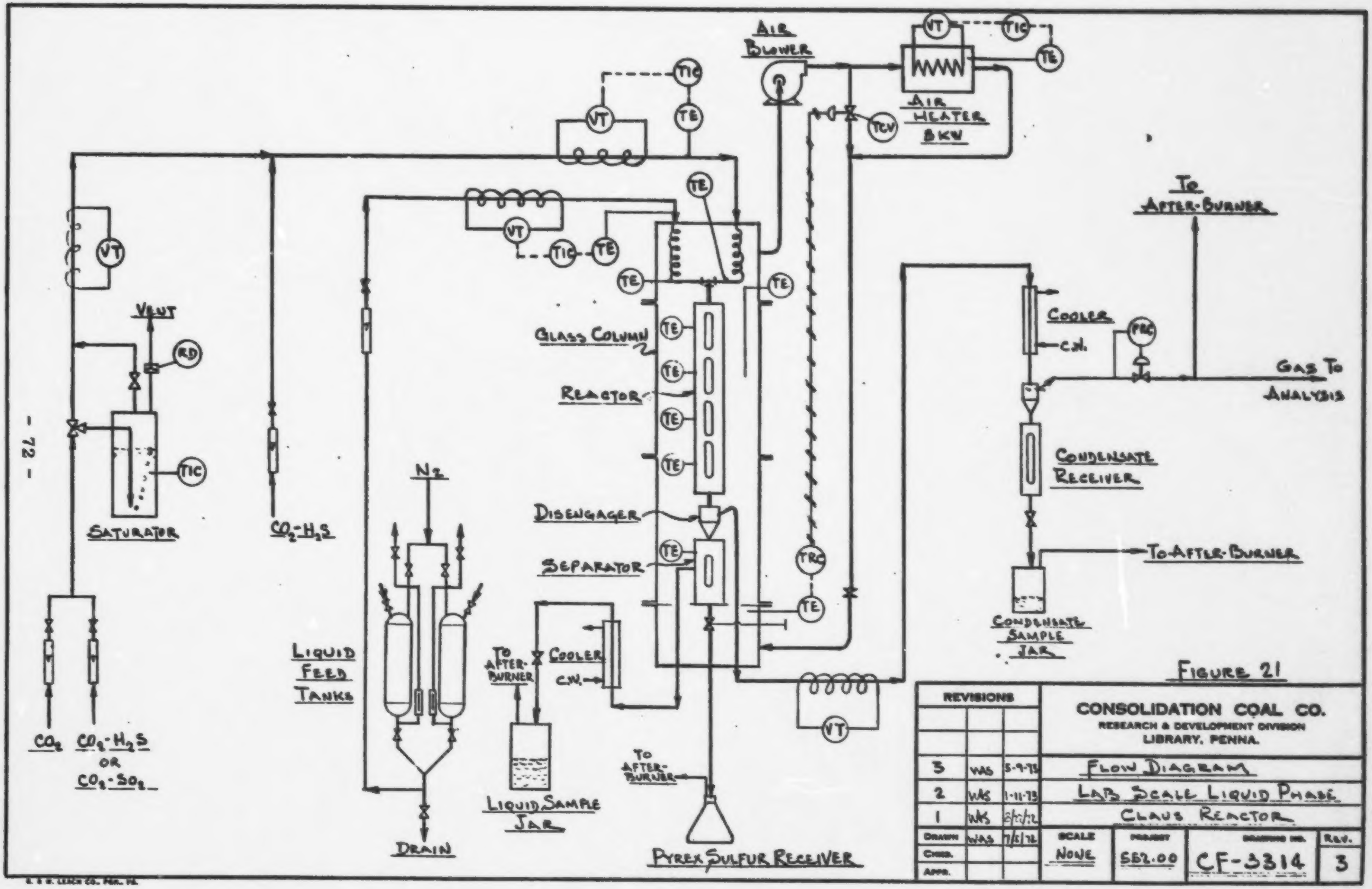
AIR BLOWER
VT
TIC
TE
AIR HEATER 8KW
TCV
TO AFTER-BURNER
TE
VT
TIC
GLASS COLUMN
REACTOR
DISENGAGER
SEPARATOR
TRC
COOLER
C.W.
PRC
GAS TO ANALYSIS
CONDENSATE RECEIVER
TO-AFTER-BURNER
CONDENSATE SAMPLE JAR
VENT
RD
SATURATOR
CO_2-H_2S
N_2
LIQUID FEED TANKS
TO AFTER-BURNER
LIQUID SAMPLE JAR
DRAIN
PYREX SULFUR RECEIVER
CO_2
CO_2-H_2S OR CO_2-SO_2

FIGURE 21

CONSOLIDATION COAL CO.
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FLOW DIAGRAM
LAB SCALE LIQUID PHASE
CLAUS REACTOR

REVISIONS		
3	WAS	5-9-73
2	WAS	1-11-73
1	WAS	8/21/72
DRAWN	WAS	7/5/72
CHKD.		
APPD.		

SCALE	PROJECT	DRAWING NO.	REV.
NONE	582.00	CF-3314	3

Very careful temperature control was needed to prevent condensation or evaporation of water at process conditions. The temperature range under study was just beyond the point of minimum viscosity of liquid sulfur which lies at 300°F. The viscosity of liquid sulfur increases very steeply as the temperature is increased above 320°F. Thus, temperature aberrations could pose problems from this source. Close control of temperature was achieved by enclosing the entire reactor in a 6" diameter by 6' tall glass column and circulating hot air at the high rate of 150 SCFM. By maintaining a constant temperature outside the reactor, there was no need for elaborate insulation and accessory heating devices.

Since condensation of liquid in either the entrance or exit lines could have resulted in the formation of sulfur which would have caused plugging, numerous thermocouples were used to monitor temperatures on these heated lines. Exit and inlet temperatures were printed out on a 24-point recorder. Temperatures inside the glass column were read out on a digital temperature indicator which had been calibrated against an ASTM thermometer.

Continuous monitoring of exit gas concentrations was provided by an infrared SO_2 analyzer. A wet iodometric volumetric analysis was used to measure and monitor H_2S concentration.

Gas mixes were prepared gravimetrically on a Mastergram Model K-100-100-500 two pan balance. The balance had a capacity of 100 KG with a sensitivity of 100 mg.

For the last three runs, the unit was repiped as shown in Figure 22. Two thermocouples were removed. The lower one was replaced with a gas inlet line terminating in a three-hole sparger, and the upper one was used as a liquid feed line. Product gas exited through the top and sulfur was withdrawn from the bottom as before. The packing in this mode was removed and the unit was operated with a pool of liquid sparged with gas.

The unit was started up by bringing it up to temperature with the large air heater, and heating the inlet and exit lines. The reactor was brought to pressure by using CO_2 at the flow rate of the mix gas. The steam generator was brought onstream, and then water was fed in. The SO_2-CO_2 mix was substituted for the inert gas and the exit gas composition was followed on the infrared analyzer. When the exit gas composition was constant, the run was started by turning on the H_2S-CO_2 mix.

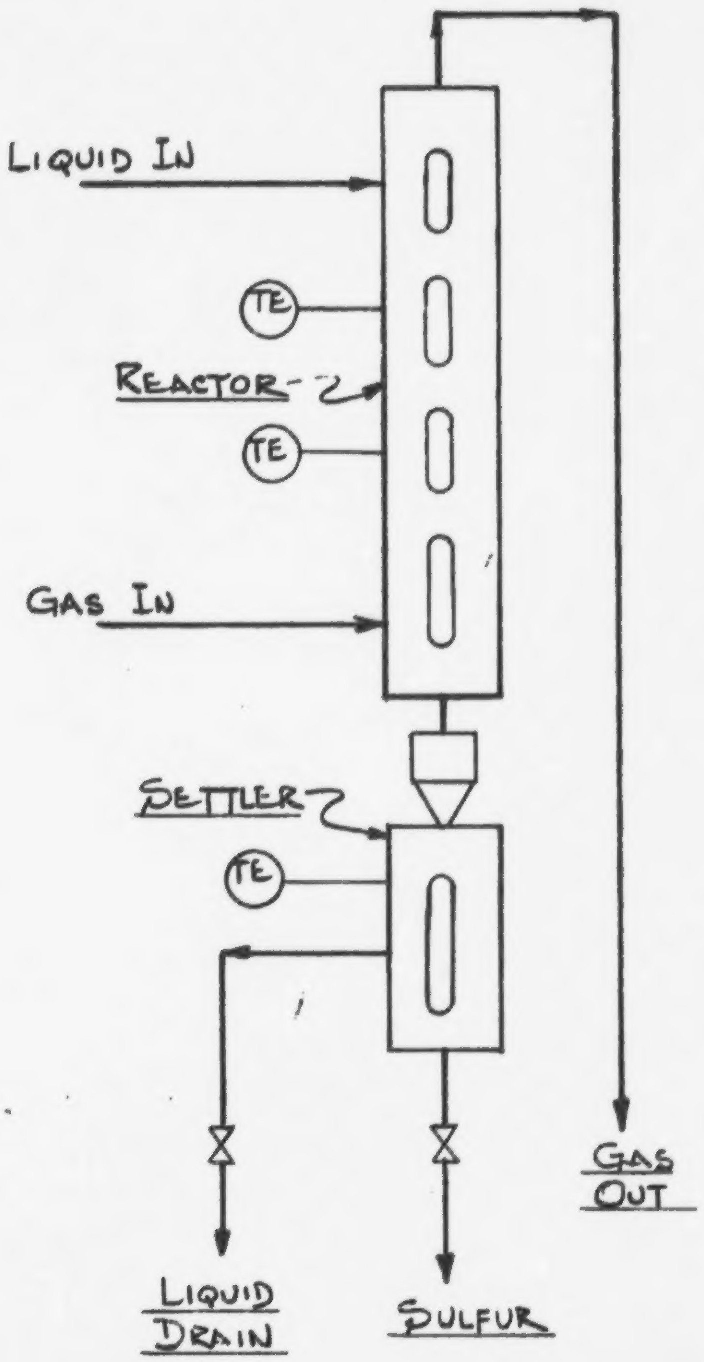
The SO_2 content of the offgas was continuously monitored with the infrared analyzer. Hourly collections of sulfur and condensate were taken and the H_2S content of the offgas was also analyzed once per hour.

For once-through operations, the product liquid was collected hourly. For recycle operation, when a feed hopper was emptied, the alternate hopper was switched onstream and the product was removed and weighed. The product was then filtered of sulfur fines and returned to the empty hopper.

The run was ended by simultaneously shutting off the flows of sulfur-bearing mixes and substituting CO_2. All the sulfur and solvent liquid were then drained from the column. CO_2 was then diverted out of the steam generator and the unit depressurized. The reactor was allowed to cool slightly before being washed with toluene followed by methanol.

FIGURE 22

LIQUID-PHASE CLAUS SYSTEM PIPED FOR BATCH LIQUID OPERATION


LIQUID IN
TE
REACTOR
TE
GAS IN
SETTLER
TE
GAS OUT
LIQUID DRAIN
SULFUR

V. MATERIALS: SOURCE, PREPARATION AND ASSAYS

A. Inert Char

The char used in the coal pretreatment studies was produced by carbonization of Kayford coal (Bethlehem Steel Mine in West Virginia) in Consolidation Coal Company's Formcoke Pilot Plant. The char was inert and completely noncaking.

The char was sized as shown in Figure 23. Properties of the 28 x 100 mesh char are presented in Table 16.

To simulate the seed char from commercial equipment (fines from the internal cyclone in a commercial CBC gasifier), -100 mesh char was used. The sieve analysis of the char is shown in Table 17.

Coal pretreatment operations were started with inert char beds.

B. Ireland Mine Coal

The coal used in the pretreatment studies was Pittsburgh Seam coal from Consolidation Coal Company's Ireland Mine. The Ireland Mine coal is a high-volatile, high-sulfur steam coal which is highly fluid when heated through the plastic temperature range of 700-900°F.

The raw coal remaining from the previous campaign was dried, ground and sized. The required sizes were obtained by the procedures shown on Figure 24. The properties are shown in Tables 18 and 19.

The first attempt to preoxidize "coarse" coal with the draft tube used 24 x 100 mesh Ireland Mine coal remaining from our 1971 campaign. The properties were published previously.(1)

C. Loveridge Char

The raw material for the demonstration and gasification kinetics runs was precarbonized char from Pittsburgh Seam coal from Northern West Virginia (Consol's Loveridge Mine) produced in Consol's Formcoke pilot plant. Char was screened at 28 x 65 mesh and was divided into three parts treated separately at 1200, 1600 and 1700°F in the unit shown in Figure 17. The treatment conditions are given in Table 20.

The part of char treated at 1200°F which was not used up in Runs D-11 and D-12 was further treated at 1400°F to eliminate the possibility of coking in Run D-13.

The chars treated at 1600 and 1700°F were used as feedstocks for the gasification kinetics runs. The fuel char used in the CBC studies was the product from the demonstration runs and gasification kinetics runs. The reason for this was to simulate as closely as possible the feedstock which would be used in a commercial application.

A block diagram showing the steps for the use of Loveridge char is in Figure 25.

Char compositions and properties after treatment are shown in Table 21.

FIGURE 23

PREPARATION OF INERT CHAR FEEDS

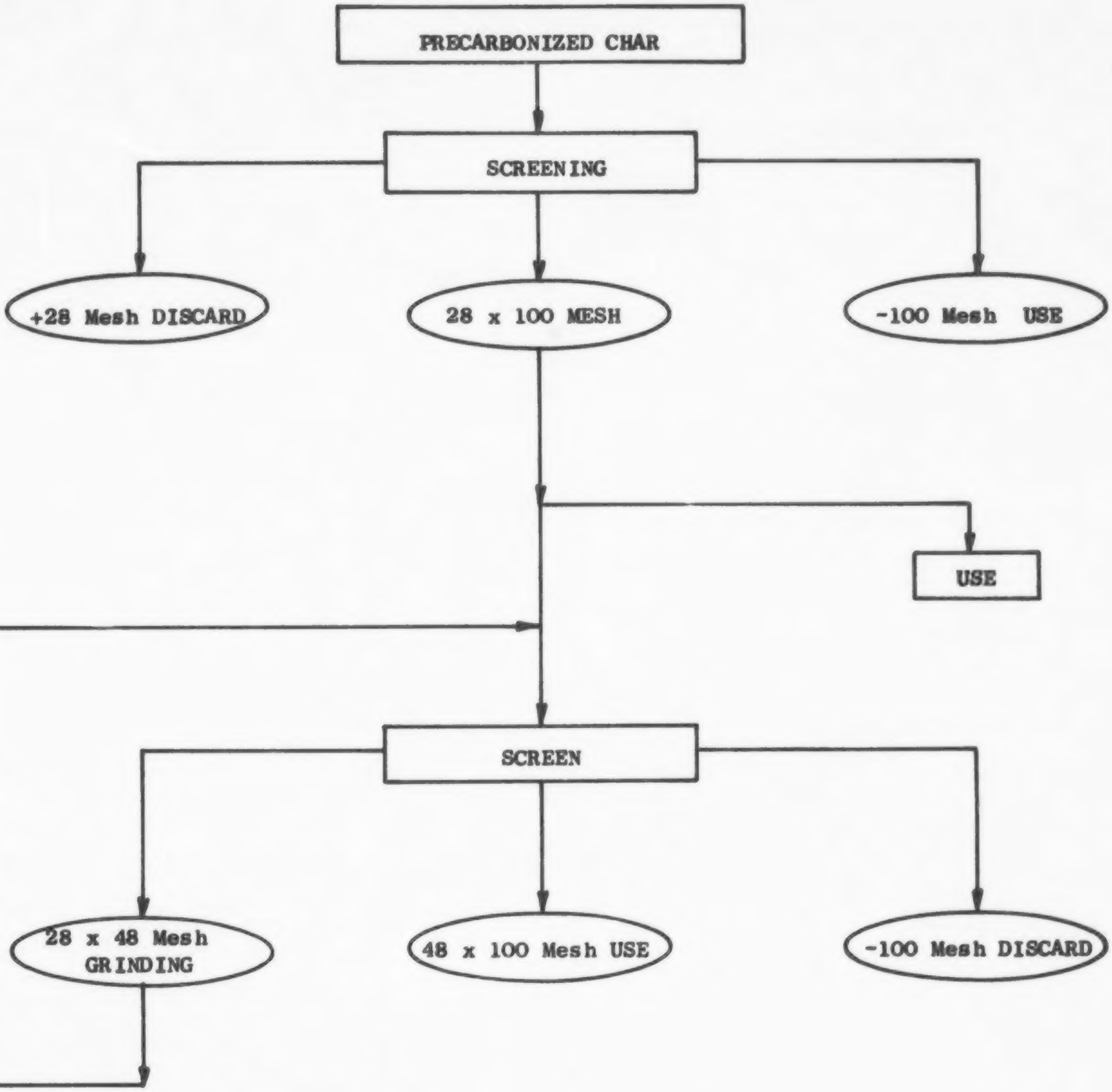

PRECARBONIZED CHAR
SCREENING
+28 Mesh DISCARD
28 x 100 MESH
-100 Mesh USE
USE
SCREEN
28 x 48 Mesh GRINDING
48 x 100 Mesh USE
-100 Mesh DISCARD

Table 16

Properties of Precarbonized Char - 28 x 100 Mesh Fraction

Hydrogen, Wt % (dry basis)	1.82
Carbon	83.7
Nitrogen	1.56
Oxygen (by difference)	2.05
Sulfur	.90
Ash	9.97
Volatile Matter	5.93
Size, Tyler Mesh, Wt %	
24 x 28	.6
28 x 35	17.0
35 x 48	38.9
48 x 65	22.8
65 x 100	17.1
-100	3.6
Mean Diameter, inches(1)	.0126
Mean Density, lb/ft^3(2)	82.5

(1) Arithmetic mean.
(2) Measured in mercury at one atmosphere.

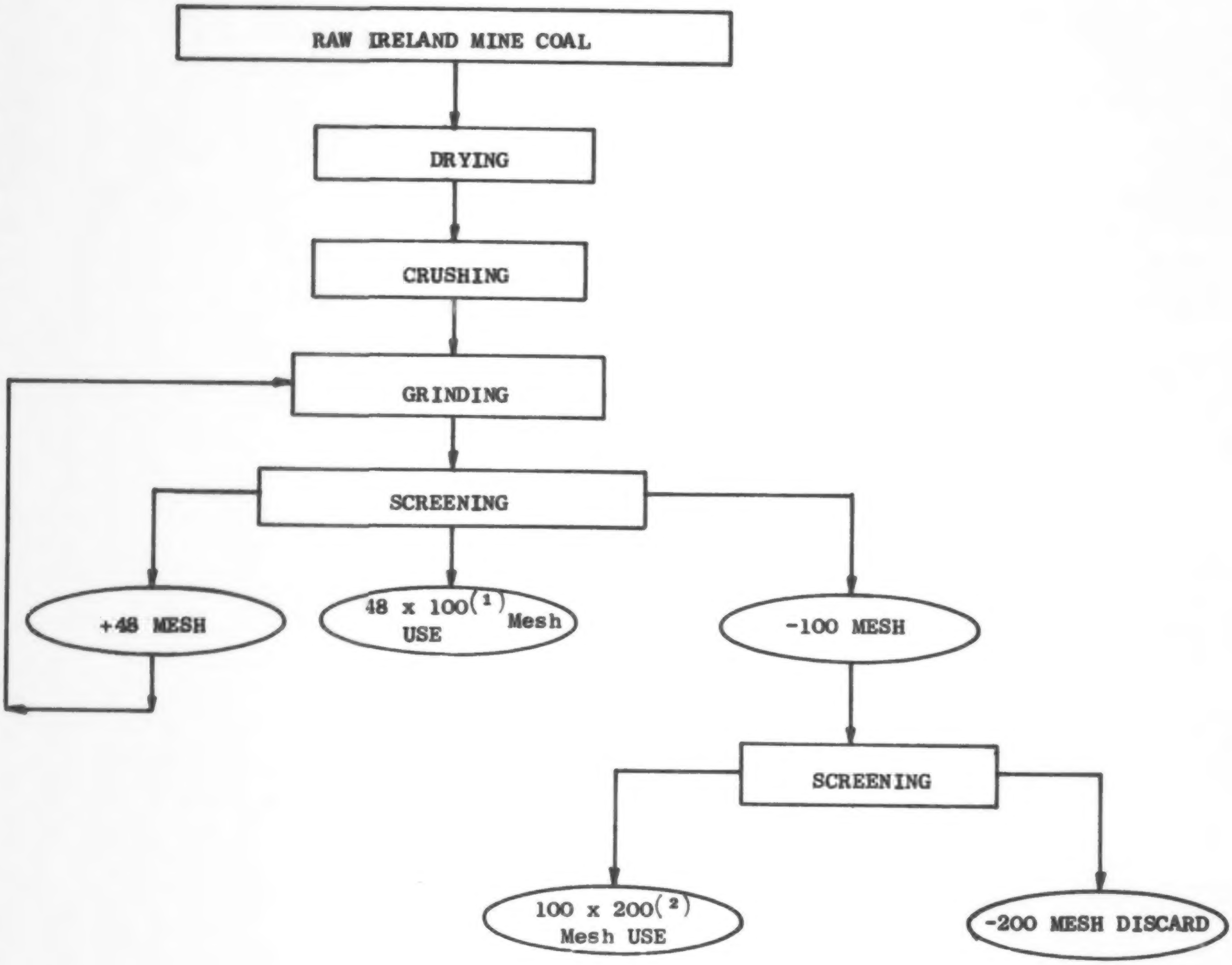
Table 17

Sieve Analysis of -100 Mesh Precarbonized Char

Size, Tyler Mesh, Wt %	
+65	.0
65 x 100	2.0
100 x 150	19.6
150 x 200	30.9
200 x 325	31.5
-325	16.0

FIGURE 24

PREPARATION OF FEED COAL


RAW IRELAND MINE COAL
DRYING
CRUSHING
GRINDING
SCREENING
+48 MESH
48 x 100(1) Mesh USE
-100 MESH
SCREENING
100 x 200(2) Mesh USE
-200 MESH DISCARD

(1) Nominal, see Table V-3 for detailed size consist.

(2) Nominal, see Table V-4 for detailed size consist.

Table 18

Properties of Feed Ireland Mine Coal

Hydrogen, Wt % (dry basis)	4.87
Carbon	69.88
Nitrogen	1.25
Oxygen (by difference)	6.69
Sulfur	4.65
Ash	12.66
Volatile Matter	41.3
Size, Tyler Mesh, Wt %	
+48	.0
48 x 65	16.1
65 x 100	71.3
100 x 150	11.4
-150	1.2
Mean Diameter, inches(1)	.00717
Mean Density, lb/ft^3(2)	82.0

(1) Arithmetic mean.
(2) Reciprocal mean, measured in mercury at one atmosphere.

Table 19

Sieve Analysis of 100 x 200 Mesh Ireland Mine Coal

Size, Tyler Mesh, Wt %	
+100	1.8
100 x 150	32.8
150 x 200	36.9
200 x 270	20.0
270 x 325	1.0
-325	7.5

Table 20

Char from Loveridge Mine Coal Treatment
Pressure: 15 Atm. (206 psig)

Feedstock	28 x 65 Mesh Loveridge Char			
Temperature, °F	1200	1400	1600	1700
Input, SCFH				
Fluidizing Gas				
N_2	90			
Recycle	160			
Lift Gas				
Air	40			
N_2	60			
Purges				
N_2	20			
Char Feed Rate, lb/hr	10			

FIGURE 25

PRETREATMENT OF LOVERIDGE MINE CHAR

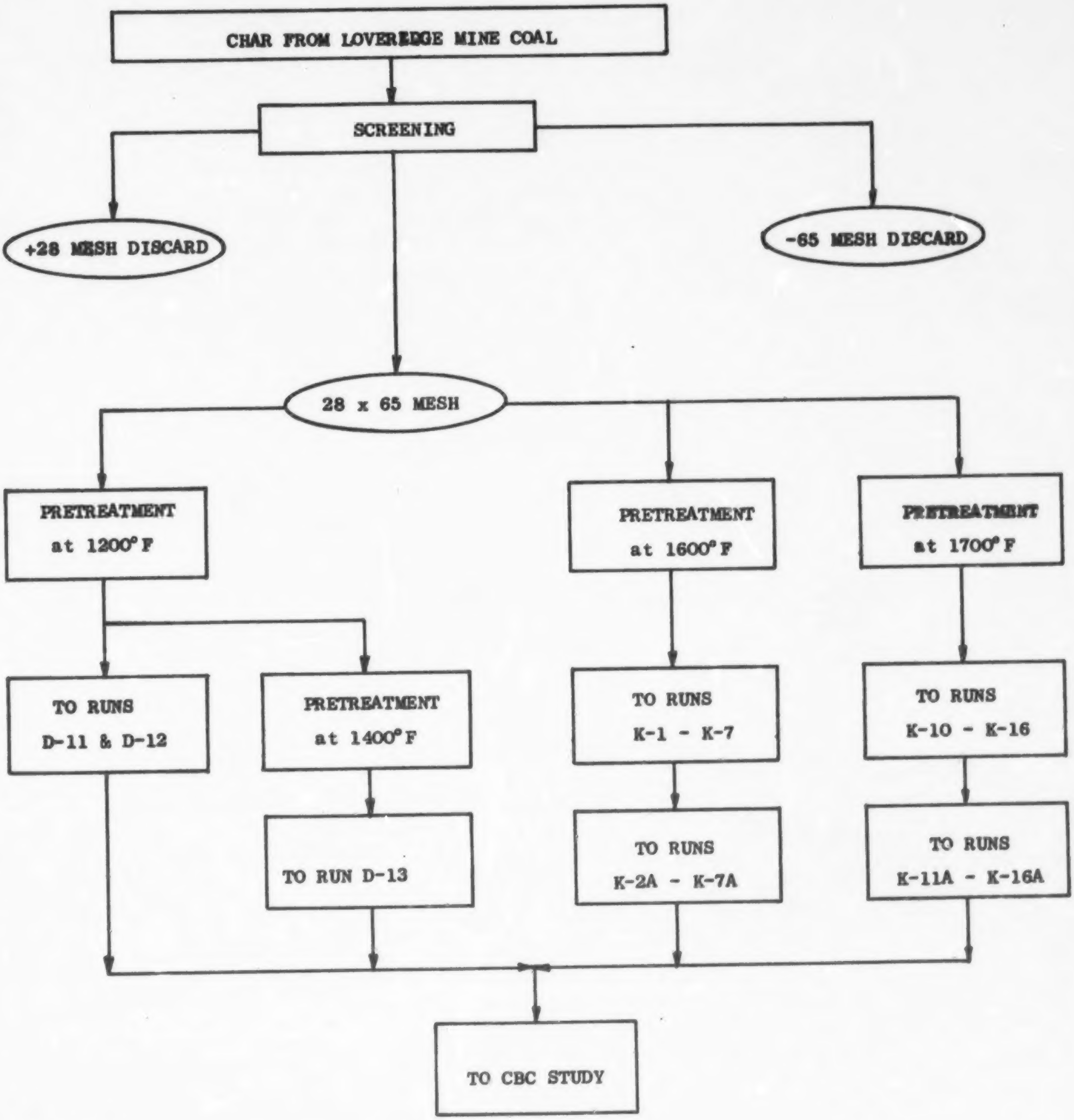

CHAR FROM LOVEREDGE MINE COAL
SCREENING
+28 MESH DISCARD
-65 MESH DISCARD
28 x 65 MESH
PRETREATMENT at 1200° F
PRETREATMENT at 1600° F
PRETREATMENT at 1700° F
TO RUNS D-11 & D-12
PRETREATMENT at 1400° F
TO RUNS K-1 - K-7
TO RUNS K-10 - K-16
TO RUN D-13
TO RUNS K-2A - K-7A
TO RUNS K-11A - K-16A
TO CBC STUDY

Table 21

Properties of Thermally Treated Loveridge Char

See Table 20 for Conditions of Treatment

Treatment Temperature, °F	1200	1400	1600	1700
H, Wt %, dry basis	1.59	1.08	.66	.52
C	80.58	82.28	84.32	84.72
N	1.32	1.60	1.24	1.32
O (diff.)	2.27	.35	-.77	-.98
S	2.09	2.13	2.03	1.85
Ash	12.15	12.56	12.50	12.63
Size, Tyler Mesh, Wt %				
+28	.5		.0	
28 x 35	19.9		17.7	
35 x 48	31.4		30.5	
48 x 65	33.3		30.9	
65 x 100	13.9		18.9	
-100	1.0		2.0	
Density of Size Fraction, lb/ft^3(1)				
28 x 35			89.4	
35 x 48			90.5	
48 x 65			89.8	
65 x 100			91.0	
-100			85.2	
Mean Density, lb/ft^3(2)			90.1	
Mean Diameter, inches(3)	.0128		.0122	

(1) Determined in mercury at 1 atmosphere.
(2) Reciprocal mean.
(3) Arithmetic mean.

D. Acceptors

During operations of the continuous acceptor unit, the following natural stones were used:

1. Tymochtee dolomite, C. E. Duff and Son, Inc.,
   Huntsville, Ohio
2. Canaan dolomite, Charles Pfizer, Inc., Adams, Mass.
3. Buchanan dolomite, James River Limestone Company,
   Buchanan, Va.
4. Pennsylvania dolomite, G. and W. H. Corson, Inc.,
   Plymouth Meeting, Pa.
5. Nebraska limestone, Hopper Brothers Quarries,
   Weeping Water, Nebraska.
6. 1691 limestone.

The composition of the stones, as used in the experimental program, are given in Tables 22 and 23.

The acceptors were ground using a mill which was adjusted to maximize the yield of the desired size fraction. The oversize fraction was reground and the undersize material was set aside. The material was then wet screened to remove all of the fines. This was necessary to make attrition data obtained in the continuous unit more meaningful. The wet screened acceptor was then dried under infrared lamps. Acceptor preparation is shown schematically in Figure 26

E. Acceptor Assays

1. Assay of Fresh Acceptors

The main purpose of the assay was to determine the useful $CaCO_3$ content of a potential acceptor. A crushed sample, sized to 28 x 48 mesh, and weighing about 25 grams was placed in a quartz tube reactor which was heated by being immersed in a fluidized sand bath furnace. After quenching to room temperature and purging with dry air, the reactor and its contents were weighed on an analytical balance after each of the following steps:

a. The sample was fluidized in CO_2 at atmospheric pressure and at 1100°F for 15 minutes. The weight loss represented the moisture content, hydrate water, the CO_2 content of unstable carbonates, one-half of the pyritic sulfur, and pyrolysis of the bitumen content. This weight loss was less than 0.5% of the raw stone for all acceptors used in the operating program.

b. The sample then was fluidized at 1 atm CO_2 partial pressure at 1550°F for 30 minutes. The weight loss represented the CO_2 content of $MgCO_3$ and the CO_2 lost during reaction of some of the $CaCO_3$ with impurities as discussed later.

Table 22

Results of Raw Stone Assays

Stone	Tymochtee Dolomite	Canaan Dolomite Run A7	Canaan Dolomite Runs A15 & A16	Pa. Dolomite	Va. Dolomite	Nebraska Limestone	BCR-1691 Limestone	Spent[2] Stone
Gravimetric Factors								
F_1	1.836	1.887	1.874	1.843	1.858	1.745	1.595	1.228
F_2	.3894	.4719	.4687	.4362	.4426	.7299	.4541	.2279
F_3[1]	.2121	.2501	.2501	.2367	.2382	.4184	.2847	.1856
Mols Useful CaO/100 lb Raw Stone	.482	.568	.568	.538	.541	.950	.647	.422

Examples:

Let W_1 = weight on $MgCO_3 \cdot CaCO_3$ basis ($CaCO_3$ basis for limestone)

W_2 = weight on $MgO \cdot CaCO_3$ basis

W_3 = weight on $MgO \cdot CaO$ basis (CaO basis for limestone)

W_s = weight of sulfided stone

y = fraction of useful Ca converted to CaS

Then, $F_1 = W_1/W_3$

$F_2 = (F_1)(F_3)$

$W_2 = (1 + F_2)\ W_1/F_1$

$W_3 = W_2/(1 + F_2)$

Mols useful Ca

in fresh, fully calcined stone = $(W_3)(F_2)/44.01$

in fresh half-calcined ($MgO \cdot CaCO_3$) stone = $(W_2)(F_2)/(1 + F_2)/44.01$

$$W_s = W_2\left[1 - (F_2)(y)(100.09 - 72.14)/44.01/(1 + F_2)\right]$$

(1) F_3 = the weight fraction of CO_2 equivalent to useful $CaCO_3$ in the raw, dry stone = $(W_2 - W_3)/W_1$.

(2) This stone originally was Tymochtee dolomite which had been exposed to many calcining-recarbonation cycles at CO_2 Acceptor Process conditions. About 42% of the original useful CaO had been converted to an inactive form.

Table 23

Compositions of Feed Acceptors

		Canaan Dolomite						
Stone	Tymochtee Dolomite	Run A7	Runs A15 & A16	Pa. Dolomite	Va. Dolomite	Nebraska Limestone	1691 Limestone	Spent(1) Stone
Useful CaO, Wt %	49.6	60.1	59.7	55.6	56.4	93.0	57.9	29.0
MgO	38.6	38.0	37.1	37.3	38.0	.6	5.5	38.6
Impurities(2)	6.8	1.8	3.2	7.1	5.6	3.3	26.4(3)	8.1
Bound CaO	4.9	.0	.0	.0	.0	3.1	10.3	3.6
							Inactive CaO	20.7

(1) See Table 22.

(2) In most stones, the impurities largely are silica and alumina. The predominant minerals indentified by x-ray diffraction, (See Reference 3) are:

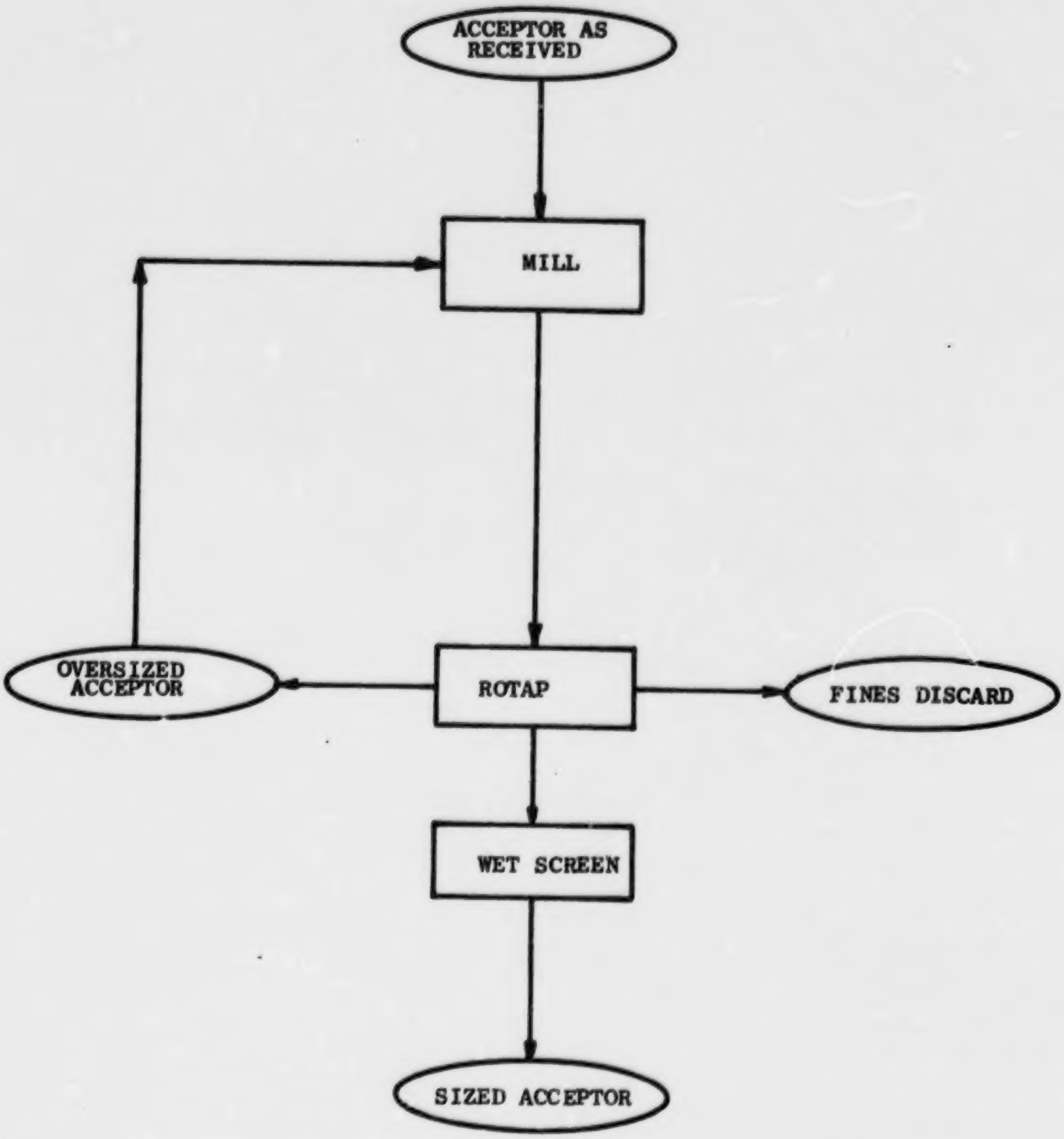
Illite	$(Na,K)O \cdot Al_2O_3 \cdot 6\ SiO_2 \cdot 2\ H_2O$
Kaolinite	$Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O$
α Quartz	

(3) The raw stone was treated with 0.5N HCl, giving an insoluble residue which amounted to 24.7% of the stone. After ignition in air, the residue composition was:

Al_2O_3, Wt %	13.5
SiO_2	75.8
Fe_2O_3	4.4
Na_2O	.2
K_2O	5.2
TiO_2	.6
P_2O_5	.2

Figure 26

Acceptor Sizing


ACCEPTOR AS RECEIVED
MILL
OVERSIZED ACCEPTOR
ROTAP
FINES DISCARD
WET SCREEN
SIZED ACCEPTOR

c. The sample then was calcined by fluidizing in N_2 at 1600°F for 30 minutes. The weight loss gave the desired useful $CaCO_3$ content of the stone.

d. The sample then was recarbonated by fluidizing in CO_2 at 1500°F for 30 minutes. This was done to complete the calcining-recarbonation cycle so that on subsequent handling the acceptor would not air-slake by reaction with atmospheric moisture. Characteristically, dolomites showed a weight gain of 95-97% of the weight loss on the previous calcining, and limestones showed 66-68%.

Supplemental tests showed that all reactions were complete in the time intervals stated above.

Except for dolomites which had very low impurity contents, the weight loss on calcining the $MgCO_3$ was greater than on calcining the $CaCO_3$. Since dolomites with a mol ratio of $MgCO_3/CaCO_3$ greater than the theoretical ratio of unity are a geological rarity, some of the $CaCO_3$ must have reacted with an impurity such as SiO_2 according to,

$$2\ CaCO_3 + SiO_2 = 2CaO \cdot SiO_2 + 2\ CO_2.$$

An experiment showed that indeed this situation had occurred: With a sample of the Tymochtee dolomite, step b was carried out at 1400°F using an 80% CO_2-20% N_2 mixture as the fluidizing gas. The exit gas composition was monitored by a thermal conductivity cell using the inlet gas as cell reference. The cell output showed that the $MgCO_3$ component had calcined completely in 15 minutes. The fluidized bed temperature then was raised to 1550°F over a period of 15 minutes. Between 1450 and 1550°F the cell output showed that incremental CO_2 appeared in the exit gas and that the reaction producing the CO_2 was completed at 1550°F. At these conditions $CaCO_3$ could not have calcined since the equilibrium temperature at 0.8 atm CO_2 partial pressure is 1617°F. The sand bath temperature was 20°F higher than the fluidized bed temperature of the acceptor. Therefore, undetected "hot spots" were not the source of the incremental CO_2.

When a direct determination of the $MgCO_3$ content was desired, step b was modified based on the above finding. The stone was fluidized in CO_2 at 1350°F for three hours in order to calcine the $MgCO_3$ while avoiding the reactions which bind some calcium to the impurities. The bound calcium then was determined from the weight loss which occurred after fluidizing in CO_2 at 1550°F for 30 minutes.

Results of the assays on the acceptors used in the operating program are given in Table 22. Two shipments of the Canaan stone were used and the results from each assay are included in the table. Gravimetric factors, calculated from the assay results are shown in the table, are useful in the conversion between the raw, half-calcined, and sulfided weights of the stone. Examples are shown in the table.

Another way of expressing the compositions of the stones used is shown in Table 23. The components shown were calculated from the various weight losses determined from assays on the raw stones. The impurity contents were obtained by difference from 100%. In earlier work,(3) the total impurity content obtained by this method always was in good agreement with results of chemical analysis for the noncalcium, magnesium components of the stones.

2. Assay of Sulfided Acceptor

To avoid the long delay in receiving the data on the CaS and $CaCO_3$ content of the recirculating acceptor after submitting the samples to the Analytical Laboratory, a special assay which could be performed by the operators was developed. The method is based on measurement of stoichiometric weight changes involved with straightforward reactions.

a. Only CaS and $CaCO_3$ Present

Usually the sample contains no CaO because the partial pressure of CO_2 is kept above the equilibrium value at all times during the sulfur cycle. Also, no $CaSO_4$ is present because this material is not stable at the reducing conditions in the gas desulfurizer. Experience has shown that CaS is not oxidized by steam or CO_2 in the regenerator at 1300°F. However, privately sponsored studies show that the oxidation rates become appreciable at temperatures above 1500°F.

A sample weighing about 20 grams was placed in a quartz tube reactor which was heated by being immersed in a fluidized sand bath furnace. The sample was fluidized in prepurified N_2 at 1400°F for 30 minutes. After quenching to room temperature and purging with dry air, the reactor and its contents were weighed on an analytical balance. The weight loss represents the $CaCO_3$ content. The composition is calculated as follows:

Let X = grams dry sample.
F_2 = gravimetric factor from assay of raw, fresh stone (see Table 22).
α = weight loss on calcining in N_2.
A = mols CaS present.
B = mols $CaCO_3$ present.
C = hypothetical sample weight if acceptor were in form of MgO·CaO.

Then,

$$C = X - \alpha - A\,(72.14 - 56.08) \qquad (1)$$

$$A + \frac{\alpha}{44.01} = C\,F_2/44.01 \qquad (2)$$

Solution of equations (1) and (2) gives

$$A = \frac{F_2\,(X-\alpha) - \alpha}{44.01 + 16.06\,F_2}$$

Also,

$$B = \frac{\alpha}{44.01}$$

Then, the composition of the acceptor, expressed as mol % of useful calcium is:

$$CaCO_3 = 100\,B/(A + B)$$
$$CaS = 100\,A/(A + B)$$

b. If $CaSO_4$ also is Present

When $CaSO_4$ purposefully has been formed during some portion of the acceptor cycle by oxidation with air, a second step is added to the assay described above. The sample is fluidized in H_2 at 1600°F for 15 minutes. After quenching to room temperature and purging with dry air, the reactor and its contents again is weighed. The weight loss represents the conversion of $CaSO_4$ to CaS.* The composition is calculated as follows:

Let ∂ = weight loss on reduction to CaS.
ϵ = factor for reducible iron content of acceptor.*
D = mols $CaSO_4$ present.
Other nomenclature as above.

Then,

$$D = (\partial - \epsilon\ C)/16/4 \qquad (3)$$

$$C = X - \alpha - A\ (16.06) - D\ (136.14 - 56.08) \qquad (4)$$

$$A + \frac{\alpha}{44.01} + D = C\ F_2/44.01 \qquad (5)$$

Solution of equations (3), (4), and (5) gives:

$$A = \frac{\dfrac{(X-\alpha)\ F_2}{44.01} - \dfrac{\alpha}{44.01} - \left[1 + \dfrac{80.06\ F_2}{44.01}\right]\left[\dfrac{\partial - \epsilon\ (X-\alpha)}{64 - 80.08\ \epsilon}\right]}{1 + \dfrac{16.06\ F_2}{44.01} + \left[1 + \dfrac{80.06\ F_2}{44.01}\right]\left[\dfrac{16.06\ \epsilon}{64 - 80.06\ \epsilon}\right]}$$

Solution of equations (3) and (4) gives

$$D = \frac{\partial - \epsilon\ (X-\alpha) + 16.06\ A\ \epsilon}{64 - 80.06\ \epsilon}$$

Also,

$$B = \frac{\alpha}{44.01}$$

Then, the composition of the acceptor, expressed as mol % of useful calcium is,

$CaCO_3$ = 100 B/(A + B + D)
CaS = 100 A/(A + B + D)
$CaSO_4$ = 100 D/(A + B + D)

---

* Most acceptors contain reducible iron which is present initially in the raw stone as limonite and pyrite. Using the same general technique as described for the raw stone assay, the raw stone was calcined by fluidizing in air at 1650°F for 30 minutes. After weighing, the sample then was fluidized in dry H_2 at 1650°F for 15 minutes. The weight loss is loss of oxygen which represents the reducible iron content. The factor, ϵ, is the ratio:

grams oxygen lost/gram of acceptor in the MgO·CaO form.

c. Refractory CaS

In the following discussion, the assumption is made that $CaSO_4$ has not been formed. The assay technique was developed using samples of freshly prepared acceptor in the form of $MgO \cdot CaCO_3$ in which a known amount of $CaCO_3$ was converted to CaS by reaction with H_2S. With these samples, the CaS content could be determined directly by the following method:

After calcining the $CaCO_3$ component in N_2 at 1400°F as described in section (a) above, the sample was fluidized in dry air as the temperature was raised from 1300 to 1600°F in 30 minutes in order to oxidize CaS to $CaSO_4$. Some generation of SO_2 always occurred by the reaction,

$$1/4 \ CaS + 3/4 \ CaSO_4 \ = \ CaO + SO_2.$$

The SO_2 was trapped in an absorption bulb containing Ascarite. After quenching to room temperature, the reactor and its contents were weighed on an analytical balance. The composition of the fresh sample was calculated as follows:

Let β = weight gain after oxidation in air.
γ = weight gain of Ascarite bulb.
other nomenclature as above.

Then,

$$A = \left(\beta + \frac{80.06}{64.06}\gamma\right) /64$$

$$B = \alpha/44.01.$$

Then, the composition of the acceptor, expressed as mol % of useful calcium is,

$$CaCO_3 = B/(A + B)$$
$$CaS = A/(A + B)$$

When samples which had been exposed to cyclical sulfiding and regeneration at process conditions were assayed by the above procedure, it was found that some of the CaS was not oxidized, even when the final temperature was increased to 1700°F and held for periods up to three hours. This unoxidized CaS has been termed "refractory CaS."

For these samples, the total CaS was calculated as in section (a) above, i.e.,

$$A = \frac{F_2 \ (X-\alpha) - \alpha}{44.01 + 16.06 \ F_2}$$

and the oxidizable CaS, A1, was calculated as

$$A1 = (\beta + \frac{80.06}{64.06} \ \gamma)/64.$$

Then, the composition of the acceptor, expressed as mol % of useful calcium is,

$$CaCO_3 = 100 \ B/(A + B)$$
$$CaS = 100 \ A1/(A + B)$$
$$\text{Refractory CaS} = 100 \ (A-A1)/(A + B)$$

VI. SAMPLE CALCULATIONS

The following operations were conducted during the course of the present contract period:

1. Preoxidation
2. Seeded Coal Pretreatment
3. Acceptor Sulfur Cycle Studies
4. Carbon Burnup Cell Tests
5. Gasifier Operability Demonstrations
6. Gasification Kinetics
7. Liquid-Phase Claus Reaction Runs

Sample calculations involving preoxidation and gasification were detailed in the last report.(1) Calculations detailing gasification kinetics are discussed in Section XII. Seeded Coal Process studies were preliminary in nature and detailed calculations were not carried out. The sample calculations in the next sections therefore discuss only Items 3, 4, and 7 above.

A. Acceptor Sulfur Cycle Studies

1. Calculation of Number of Process Cycles

Definition of a Cycle

A cycle is completed when the entire inventory of acceptor has passed through the gas desulfurizer. The inventory consists of the contents of the gas desulfurizer, regenerator and their respective acceptor transfer lines together with the acceptor in the feed hoppers and product receivers.

$$\Delta N = \frac{\Delta H}{I + X} \quad \text{evaluated from } t \text{ to } t + \Delta t.$$

where: ΔN = change in number of cycles accumulated.

ΔH = grams of half-calcined acceptor fed during the period.

I = average internal inventory of reactors and transfer lines over the period, grams.

X = average external inventory of acceptor over the period, grams.

$t, \Delta t$ = time and time increments, respectively.

The external inventory changes due to attrition and sampling losses. There is a loss of weight in both the external and internal inventory as $CaCO_3$ (MW 100.1) is replaced by CaS (MW 72.1).

Fractional cycles exist when only part of the inventory has been through the reactor. Let n + f be the number of cycles, where n is an integer and f is the fraction of the inventory which has come out of the gas desulfurizer. On the average, f part of the inventory has seen n + 1 cycles, and 1 - f has seen n cycles. In our system the mixing occurring in the fluidized beds and in the product collection pot brings about smooth changes in the sulfur content of the acceptor. Average cycles are used; no attempt has been made to define a residence time distribution for the experimental system.

All the data, including regenerator analyses are keyed to the gas desulfurizer. Generally, about 1/4 to 1/3 of the total inventory is in the regenerator. Thus, the material exiting the regenerator is about 1/4 of a cycle "younger" than the material leaving the gas desulfurizer. In the figures which plot CaS content of acceptor as a function of cycles, the regenerator curve is displaced about 0.25 cycles to the right from the gas desulfurizer curve for purposes of comparing the change in a given acceptor particle.

Sample Calculation of Process Cycles - Run A7

The number of process cycles was calculated over periods of time corresponding to about 9,000 grams of feeding. From 384 to 525 minutes into the run, 9,063 grams of acceptor were fed. During this period, the feed hoppers were switched six times. At the instant that a feed hopper is started the external inventory consists of the contents of that feed hopper plus the contents of the full acceptor collection hopper. Thus, the external inventory is the average of two feed hoppers during the period. Therefore, from 366 to 507 minutes into Run A7,

$$\text{External inventory} = X = \frac{9063}{6/2} = 3{,}021 \text{ grams.}$$

In Run A7, the beds were removed from the reactors just after the half-calcining period and again at the end of the run. The weights were 3,862 grams and 3,500 grams, respectively. A smooth curve was drawn between the points and the average internal inventory was estimated from the curve for each calculation. The change in internal inventory was small compared to the total inventory.

From 366 to 507 minutes into the run,

$$\text{Internal inventory,} \quad I = 3{,}700 \text{ grams,}$$

$$\text{and} \quad I + X = 3{,}700 + 3{,}021 = 6{,}721 \text{ grams.}$$

$$\text{Change in number of cycles} = \Delta N = \frac{\Delta H}{I + X} = \frac{9{,}063}{6{,}721} = 1.35$$

At the start of the period, 2.83 cycles had been accumulated. Therefore, the number of cycles at the end of the period was:

$$\Sigma N = 2.83 + 1.35 = 4.18 \text{ cycles.}$$

For Run A7, the calculations are summarized in Table 24.

2. Calculations of Conditions and Results for Gas Desulfurizer - Run A7

The numbers used below were taken from Run A7. See Tables 44 and 45 in Section IX.

Gas Desulfurizer Temperature

Axial temperature traverses showed that the gas desulfurizer bed temperature was constant to ± 2°F over the entire length of the acceptor bed. The bed temperature was continuously measured by thermocouples positioned 1" and 15" above the bottom of the bed.

Table 24

Computation of Number of Cycles-Run A7

Time, Minutes		ΔH, Acceptor Fed, Grams	n, Number of Hopper Changes	$X = \frac{\Delta H}{n/2}$, External Inventory, Grams	I, Internal Inventory, Grams	I + X, Total Inventory, Grams	$\Delta N = \frac{\Delta H}{I + X}$, Change in Number of Cycles	$\Sigma \Delta N$ = Total Number of Cycles
Start	End							
0	229	11853	6	3951	3815	7766	1.53	1.53
229	384	10023	6	3928(1)	3740	7668	1.30	2.83
384	525	9063	6	3021	3700	6721	1.35	4.18
525	737	10626	8	2657	3655	6312	1.64	5.82
737	919	9177	8	2294	3610	5904	1.55	7.37
919	1081	7551	8	1888	3580	5468	1.38	8.75
1081	1260	8386	10	1677	3550	5227	1.60	10.35
1260	1412	7191	10	1438	3525	4963	1.45	11.80
1412	1531	5698	9	1226	3510	4776	1.19	12.99

(1) Part of hopper fed during restart of unit. $X = 11785/3 = 3928$.

Acceptor Feed Rate

Over the first 203 minutes of the run, 9,989 grams of half-calcined acceptor were fed. The feed rate was calculated as,

$$\frac{9,989 \times 60}{203} = 2,952 \text{ gm/hr} = 6.50 \text{ lb/hr}.$$

Solids Retention Time

The bed height is 1.5 feet and the diameter is 3 inches. The solids occupies 0.35 of the volume and has a density of 135 lb/ft^3. The weight of acceptor in the bed is therefore,

$$0.785 \times \frac{9}{144} \times 1.5 \times 0.35 \times 135 = 3.47 \text{ lbs}.$$

Since the feed rate was 6.5 lb/hr, the nominal residence time in the bed is,

$$\frac{3.47 \times 60}{6.50} = 32 \text{ minutes}.$$

Exit Gas Composition

The exit gas composition was determined directly from the iodometric H_2S analysis and the GC analysis of the offgas. In the absence of the GC analysis, the exit composition was calculated from the inlet flows and the condensate collection. The inlet gas contained excess CO_2 and H_2. Experience has shown that shift equilibrium is rapidly achieved at the bottom of the reactor. CO and H_2O are produced via the shift reaction. The desulfurization reaction consumes H_2S and produces additional CO_2 and H_2O.

Over three hours, 2,568 grams of condensate were collected for an average hourly rate of 856 gm/hr. Converting to SCFH,

$$\frac{856 \times 387}{18.02 \times 454} = 40.5 \text{ SCFH of } H_2O.$$

Via dry gas meter readings, the dry exit gas rate converted to standard conditions was 220 SCFH. Iodine scrubber analysis showed the H_2S concentration to be 0.049%. Then,

$$H_2S \text{ reacted} = 3.5 - .00049 \times 220 = 3.4 \text{ SCFH}.$$

Since each cubic foot of H_2S which reacts generates one cubic foot each of CO_2 and H_2O, the net water formed via the shift reaction was 37.1 SCFH. The dry exit gas rate may be estimated as follows:

H_2S or Product CO_2	3.5 SCFH
Inlet CO_2	54
Inlet H_2	73
Inlet N_2	96
Purges (5 CO_2, 15 N_2)	20
Less H_2O via Shift	-37.1
Total Dry Gas	209.4 SCFH

The calculated and observed exit gas rates agreed within 5%. The average of 215 SCFH was taken as the actual dry exit gas rate, and the material balance value was used for calculational purposes. The contents of the exit and recycle flows were calculated as shown below:

Compound	Inlet	Shift	Reaction	Purge	Exit Gas via Material Balance SCFH (209.4)		Actual Exit Gas, SCFH (215)	Recycle, SCFH (175)
					SCFH (209.4)	Mol %		
H_2S, .049%					.1054	.049	.1078	.08575
CO_2	54	-37.1	3.4	5	25.3	12.1	26.0	21.2
H_2	73	-37.1			35.9	17.1	36.8	29.9
N_2	96			15	111.0	53.0	114.0	92.8
CO		37.1			37.1	17.7	38.1	31.0

In those cases where the GC analysis was available, the SCFH of each component in the recycle gas and the exit gas was obtained by multiplying the mole fraction by the gas flow rate.

Gas Flow and Composition Above the Bed

The total flow above the bed = dry exit flow + recycle + steam - purges above the bed. Thus, the total flow above the bed was,

$$215 + 175 + 40.5 - 15 = 415.5 \text{ SCFH.}$$

On a wet basis just above the bed we get,

Component	SCFH	Mol %
H_2O	40.5	9.75
CO_2	47.2	11.4
H_2	66.7	16.1
N_2	191.8	46.2
CO	69.1	16.6
H_2S	.1912	.046

Fluidizing Velocity

The general equation for the fluidizing velocity is as follows:

$$V = \frac{Q}{3600} \times \frac{144}{A} \times \frac{1}{\pi} \times \frac{T}{530}$$

$$\text{or} \quad V = 7.55 \times 10^{-5} \frac{QT}{A\pi}$$

where:
V = fluidizing velocity, ft/sec.
Q = gas flow rate, SCFH.
A = cross-sectional area of vessel, in^2.
T = bed temperature, °R.
π = system pressure, atm.

The cross-sectional area of the reactor was 7.24 in^2. Thus,

$$\frac{7.55 \times 10^{-5} \times 2060 \times 416}{7.24 \times 15} = 0.60 \text{ ft/sec.}$$

Approach to Equilibrium

The equilibrium ratio for $P_{H_2O} \times P_{CO_2}/P_{H_2S}$ is 510 at 1600°F. This may be expressed in mol fractions as,

$$510 = \frac{X_{H_2O} \times 15 \times X_{CO_2} \times 15}{X_{H_2S} \times 15}$$

where the subscripted X represents a mol fraction. The equilibrium mol % H_2S was,

$$\% \; H_2S \; = \frac{100 \times X_{H_2O} \times X_{CO_2} \times 15}{510} = \frac{100 \times .0075 \times .114 \times 15}{510} = .0327\%.$$

Since the percent of H_2S above the bed was .046,

$$\% \; H_2S \text{ in Outlet/Equilibrium } \% \; H_2S = .046/.0327 = 1.4.$$

Removal of H_2S

The percentage removal of fresh H_2S was,

$$\text{Removal of Feed Sulfur} = 100 \times \frac{(3.5 - .108)}{3.5} = 97\%.$$

The percentage removal of feed plus recycle H_2S was,

$$\text{Removal of Feed + Recycle } H_2S = 100 \times \frac{(3.5 - .108)}{3.5 + .0875} = 95\%.$$

Conversion of Acceptor

$$\text{Mols of } H_2S \text{ reacted} = \frac{3.5 - .108}{386.8} = .00877.$$

The molar feed rate of acceptor was calculated by first converting the feed rate to the raw stone basis and then dividing by the pounds raw stone per mol Ca using the gravimetric factors given in Section V-E.

$$\text{Mols of Useful Ca Fed} = \frac{\text{Feed} \times F_1 \times \text{Mols Ca/100 lb Raw Stone}}{(1 + F_2) \times 100} = \frac{6.50 \times 1.887 \times .568}{(1 + .4719) \times 100}$$

$$= .04735$$

$$\text{Conversion of Acceptor} = 100 \times \frac{.00877}{.04735} = 18.52\%.$$

Rate of Attrition

Including the calcining period, a total of 96,348 grams of acceptor were fed to the unit. The solids filters yielded 773 grams from the gas desulfurizer and 25 grams from the regenerator. The overall attrition rate was,

$$\text{Attrition Rate} = \frac{(773 + 25) \times 100}{96,348} = .83\%.$$

3. Calculation of Conditions and Results for Regenerator - Run A7

Regenerator Temperature

Axial temperature traverses showed that the regenerator bed temperature was constant to within 2°F over the entire length of the acceptor bed. The bed temperature was continuously measured by thermocouples positioned 16", 21", and 42" above the bottom of the bed.

Solids Retention Time

The bed height was 46" and the diameter was 2". The solids occupied .35 of the volume and had a density of 135 lb/ft^3. The weight of acceptor in the bed was therefore,

$$.785 \times \frac{4}{144} \times \frac{46}{12} \times .35 \times 135 = 3.96 \text{ lbs}$$

Since the feed rate was 6.5 lb/hr, the nominal residence time in the bed was,

$$\frac{3.96 \times 60}{6.50} = 37 \text{ minutes}$$

Exit Gas Composition

The exit gas analysis is determined directly from the iodometric H_2S analysis and the GC analysis of the offgas. In the absence of the GC analysis, the exit composition was calculated from the inlet flows and the condensate collection as follows. Over three hours an average of 2324 gm/hr of condensate was collected. Converting to SCFH,

$$\frac{2324 \times 387}{18.02 \times 454} = 110 \text{ SCFH}$$

Via the dry gas meter, the dry exit gas rate converted to standard conditions was 133 SCFH. Iodine scrubber analyses showed the H_2S concentration to be 0.7%. Then,

$$H_2S \text{ released} = .007 \times 133 = .93 \text{ SCFH}$$

Each cubic foot of H_2S released consumed one cubic foot each of CO_2 and H_2O.

The dry exit gas rate may be estimated as follows:

CO_2 or Product H_2S	110 SCFH
Purges (5 CO_2, 18 N_2)	23
Total Dry Gas	133 SCFH

The calculated and observed exit gas rates were in excellent agreement.

The composition of the exit flow was calculated as shown below:

Compound	Inlet	Reaction	Purge	SCFH	Mol %
CO_2	110	-1	5	114	85.7
N_2			18	18	13.5
H_2S		.93		.93	.7

Gas Flow and Composition Above the Bed

The total flow above the bed = dry exit flow + steam - purges above the bed. Thus, the total flow above the bed was,

$$133 + 110 - 15 = 228 \text{ SCFH}.$$

On a wet basis above the bed we get:

Component	SCFH	Mol %
CO_2	109	57.8
H_2S	.93	.41
H_2O	110	48.3
N_2	8	3.5

Fluidizing Velocity

The area of the reactor is 3.20 in^2. Thus, the fluidizing velocity is,

$$\frac{7.55 \times 10^{-5} \times 1760 \times 228}{3.20 \times 15} = .63 \text{ ft/sec.}$$

Conversion of Acceptor

The exit gas contained .93 SCFH of H_2S or .0024 mols. The acceptor feed rate was .04735 mols/hr. The regeneration of acceptor was,

$$.0024/.04735 = 5.1\%.$$

B. Carbon Burn-up Reactor Calculations - Run CBC-8, Phase 2

Reactor Temperature and Temperature Gradient

Traverses of the reactor at two times are shown in Figure 27. The target temperature for the run was 1900°F, and the run temperature was taken as the maximum temperature in the bed. The recorded maximum temperature actually varied by 6°F higher and lower than the target temperature. The gradient was the difference between the bottom of the bed and the temperature 16" above the bottom. The nominal bed height was 18", but it was felt that fluctuations in bed height might leave this point uncovered at times thereby giving an inaccurate value for the bed temperature. The reported temperature gradient of 22°F was the mean of 21 determinations with a range of 10-30°F.

Char Feed - Run CBC8, Phase 2

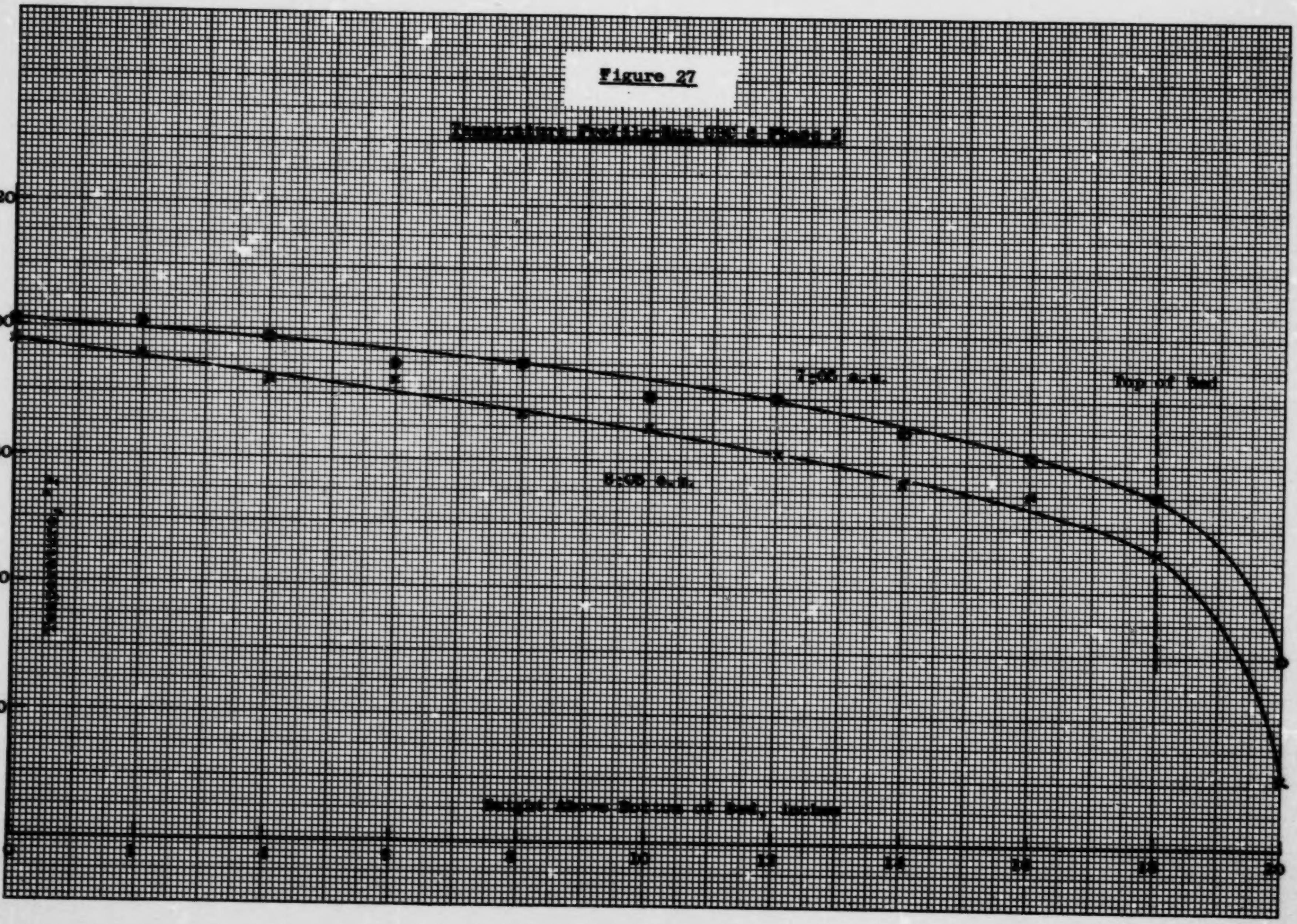
Char was fed at the rate of 1.41 lb/hr. The components of the char and their fate relative to oxidation are shown in the table below:

Component	lb/hr	SCFH	Product Gas, SCFH	O_2 Consumed, SCFH
Moisture	.00505	.11	.11	0
Ash	.226			
H_2	.00688	1.32	1.32	.66
C	1.135	36.55	36.55	36.55
N_2	.0105	.14	.14	0
S	.0237	.29	.29	.29
Total	1.407		38.4	37.5

K+E 10 X 10 TO ½ INCH 46 1323
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

Figure 27

Temperature Profile-Run [illegible] Phase 2



Composition of Exit Gas

The composition of the exit gas streams was determined by material balance as shown below. Analysis of the overhead solids showed that all combustibles in the char had been burned up.

Compound	In, SCFH	From Char, SCFH	Top of Bed		Dry + Purges Above Bed	
			SCFH	Percent	SCFH	Percent
H_2O	169	1	170	28.6	0	0
O_2	88.2	-37.5	5	8.6	5	11.5
N_2	336.8	0.1	337	56.6	357	80.2
CO_2	0	36.6	37	6.22	37	8.3
Total	594		595		445	

Oxygen Partial Pressure

The inlet oxygen partial pressure was,

$$\frac{88.2 \times 15}{594} = 2.23 \text{ atm.}$$

The exit oxygen partial pressure above the bed was,

$$\frac{51 \times 15}{595} = 1.29 \text{ atm.}$$

C. Liquid-Phase Claus Reactor - Run C6

Temperature

The temperature in the column was measured with four thermocouples. There was generally a 2°F difference between the top and the bottom of the column. The average temperature was used. In Run C6 the temperature was 310°F.

Inlet Gas Composition

The first inlet gas stream was a CO_2-SO_2 mix which was humidified in the steam generator. The temperature was set for 318°F. At the exit of the steam generator, the second gas mix containing H_2S in CO_2 was added to give the composition shown below. The dew point of the mix was 310°F.

Compound	SCFH	Mol %
H_2O	10.2	35.4
CO_2	17.0	59.0
H_2S	1.086	3.77
SO_2	.543	1.88
Total	28.83	

The reactor cross-section was 5/8" x 3/4", so that the area was 3.26×10^{-3} sq ft. The throughput rate was,

$$\frac{28.83}{3.26 \times 10^{-3}} = 8840 \text{ SCFH/ft}^2$$

Solvent Liquor Rates

Over a 45-minute period, a hopper containing 442.2 grams of recycle liquor was fed for an hourly rate of 590 gm/hr. This corresponded to 1.30 lb/hr or,

$$\frac{1.30}{3.26 \times 10^{-3}} = 400 \text{ lb/hr-ft}^2$$

Over the same time period, 453.6 gm or 604.8 gm/hr of product liquor were collected. This corresponds to 1.33 lb/hr.

Elemental Sulfur Product Rate

The collection of elemental sulfur tended to be irregular, and the product rate was taken as the average hourly rate over the last 5.9 hours of the run. In Run C6 this was 40.9 gm/hr.

Condensate Collection

The condensate was actually Wackenroder's solution since it contained sulfur and various soluble sulfur compounds formed from the low temperature reaction of H_2S and SO_2 in liquid water. The condensate was collected hourly. For Run C6, the rate was 196.4 gm/hr and the sulfur content of the condensate was 3.87%.

Exit Gas Composition

Since sulfur compounds were removed from the exit gas as the condensate was formed, the sulfur content of the gas was useful only for material balance calculations. In Run C6 the exit gas rate was 17.2 SCFH and contained 1.3% H_2S together with 0.1% SO_2.

Sulfur Balance

The sulfur balance for Run C6 is outlined below:

Component	Calculation	Grams of Sulfur/hr	Percent
Feed Sulfur			
Feed H_2S	$1.086 \times \frac{454}{387} \times 32.06$	40.8	66.0
Feed SO_2	$.543 \times \frac{454}{387} \times 32.06$	20.4	33.0
Solvent Liquor	590 x .0011	.65	1.0
Total Feed Sulfur		61.85	
Exit Sulfur			
Product Liquor	604.8 x .0011	.665	1.08
Exit Gas	$17.2 \times (.013 + .001) \times \frac{454}{387} \times 32.06$	9.06	14.6
Condensate	196.4 x .0387	7.60	12.3
Elemental Product Sulfur		40.9	66.1
Losses and Accumulation (by difference)		3.63	5.9

The losses and accumulation entry merely brings the material balance to 100%. However, losses do occur in both the sulfur exit piping and in the condensate receiver as these contain sulfur when they are examined at the end of the run. It is believed that the sulfur analysis of the condensate may be low because of the difficulty of removing the solid sulfur when an aliquot sample is taken.

VII. TABULAR CHRONOLOGICAL HISTORY OF RUNS

The purpose, general run conditions, and major conclusions drawn for all runs made in the course of this contract period are given in the tables listed below. All the runs were made at a pressure of 15 atmospheres.

TABLE NO.	
25	Summary of Seeded Coal Tests
26	Summary of Proxidizer Operations
27	Summary of Sulfur Acceptor Runs
28	Summary of Gasifier Demonstration Runs
29	Summary of Gasifier Kinetics Runs
30	Liquid-Phase Claus Reaction Operations
31	Carbon Burn-up Cell Operations

Table 25

Summary of Seeded Coal Tests

Run Number	1-5	6-19	20-23
Draft Tube Configuration	A	B	C
Date of Runs	1, 4/12/72 2-5, 4/13/72	6-8, 4/17/72 9-10, 4/18/72 11-14, 4/20/72 15-19, 4/21/72	20-22, 4/26/72 23, 4/28/72
Purpose of Runs	Exploratory	Operate with larger tube having coal feed line inside	Try accelerating gas to improve mixing
Size of Bed Char	28 x 100	28 x 100	48 x 100
Size of Seed Char	28 x 100	28 x 100, 48 x 100	48 x 100
Temperature Range, °F	1200-1400	1100-1500	1100-1500
Results and Conclusions	1. Poor mixing suspected. 2. Best result with 10:1 seed char to coal ratio.	1. No significant improvement. 2. Mouth of tube often choked with agglomerates. 3. 1500°F not operable	1. No significant change. 2. Concluded that most of fluidizing gas was entering draft tube.

Run Number	24-30	31
Draft Tube Configuration	D	D
Date of Runs	24, 6/2/72 25-30, 6/6/72	6/6/72
Purpose of Runs	Operate with baffles to improve mixing and fluidization	Make a long run to get steady-state product
Size of Bed Char	48 x 100	-100
Size of Seed Char	None	-100
Temperature Range, °F	900-1500	1300
Results and Conclusions	1. Little or no smearing at 900°F. 2. Caking at 1500°F. 3. Best smearing at 1300. 4. Product density > 80 lb/ft^3. 5. Agglomerates formed in all cases.	1. Maximum agglomerates 24 mesh. 2. Plug in outlet system prevented completion of run.

Table 26

Summary of Preoxidizer Operations

Run Number	PRO	PR1A	PR1B
Unit Revisions	Configuration A draft tube installed	No draft tube	Configuration D draft tube installed
Date of Run	4/6/72	5/15-16/72	5/26/72
Run Duration, hours	.17	14.1	2.0
Purpose of Run	Does draft tube allow operation at 850°F	First stage preoxidation	Second stage of preoxidation
Temperature, °F	850	675	775
Feedstock	24 x 100 Ireland Mine Coal	48 x 150 Ireland Mine Coal	PR1A Product
Shutdowns	Bed agglomerated	Voluntary	Voluntary
Results and Conclusions	1. Draft tube does not enhance operability enough to allow 850°F preoxidizer operation. 2. 8.6% preoxidation.	1. 5.7% preoxidation.	1. Run was operable. 2. 5.7% preoxidation. 3. Lab test showed product to be unsuitable gasifier feed.

Table 27

Summary of Sulfur Acceptor Runs

Run Number	A1	A2	A4
Unit Revisions	None	Changed coil and inlet line to 446 S.S.	None
Date of Run	8/3/72	8/10/72	8/18/72
Run Duration with H_2S Feed, hours	6.1	2.6	7.1
Purpose of Run	First exploratory acceptor run	Repeat A1. Refine control of wall temperature in desulfurizer and reduce gas velocity in regenerator.	Feed air into regenerator to induce $CaSO_4$-CaS Transient liquid hardening of acceptor.
Feedstock	28 x 35 Tymochtee dolomite		35 x 48 Tymochtee dolomite
Shutdowns	Had high ΔP in unit and could not switch solids filters.	Loss of acceptor inventory due to attrition	
Results and Conclusions	1. Good removal of H_2S in gas desulfurizer. 2. Only partial regeneration. CaS built up in acceptor 3. 2.5% attrition rate.	1. Confirm good H_2S removal in desulfurizer and build up of CaS. 2. 18% attrition rate.	1. 5.6% attrition. Better than A2, but worse than A1.

Run Number	A5	A6	A7
Unit Revisions	None	None	None
Date of Run	8/22/72	8/25, 31, 9/1/72	9/7, 8/72
Run Duration with H_2S Feed, hours	5.7	24.9	25.2
Purpose of Run	Determine attrition resistance of limestone	Run with dolomite known to be hard to see if sulfur cycle causes weakness	Test attrition and reactivity of Canaan dolomite
Feedstock	28 x 48 Nebraska Limestone	20 x 35 deactivated dolomite ex OCR studies	28 x 35 Canaan dolomite
Shutdowns	Voluntary	8/25 plug in L-5 then difficulty with H_2S feed 9/1 Voluntary	Voluntary
Results and Conclusions	1. Only 0.4% attrition, but little reaction with H_2S.	1. Acceptor stayed hard. Sulfur cycle per se does not cause softening.	1. Achieved only 0.7% attrition with good H_2S removal. 2. CaS accumulated in acceptor. At end, 13 mol % of acceptor/pass was being regenerated.

Run Number	A8	A9	A11
Unit Revisions	Only desulfurizer in operation		Returned to 2 vessel operation
Date of Run	9/11/72	9/12/72	10/3/72
Run Duration with H_2S Feed, hours	9.6	10.1	5.2
Purpose of Run	Examine once-through operation		Test other dolomites for attrition and activity
Feedstock	28 x 48 Tymochtee Dolomite		28 x 35 Pa. dolomite
Shutdowns	Voluntary		Loss of inventory due to attrition
Results and Conclusions	1. 86% solid conversion, 96% desulfurization. 2. Once-through operation with 85-95% solid conversion is feasible.	1. 95% solid conversion, 89% desulfurization.	1. 9.0% attrition, good activity.

Table 27 (Cont'd.)

Summary of Sulfur Acceptor Runs

Run Number	A12	A13	A15
Unit Revisions	None	None	All internals made of 310 SS changed to 446 SS. Replaced 310 SS inner shell
Date of Run	10/5, 10/72	10/11, 12/72	10/16-18/72
Run Duration with H_2S Feed, hours	15.1	19.3	35.1
Purpose of Run	Test other dolomites for attrition and activity.	Examine attrition and reactivity of a second limestone.	Run Canaan dolomite with 1100°F regenerator.
Feedstock	28 x 35 Buchanan dolomite	28 x 35 BCR 1691 Limestone.	28 x 35 Canaan dolomite
Shutdowns	10/5 Could not switch solids filters. 10/10 Loss of inventory due to attrition.	Could not transfer solids from gas desulfurizer to regenerator.	Voluntary
Results and Conclusions	1. 4.1% attrition, good activity.	1. Stone formed agglomerates. 2. 0.6% attrition with fairly good activity toward H_2S.	1. Only 7% regeneration per pass after CaS had accumulated.

Run Number	A16	A17	A18
Unit Revisions	None	Only gas desulfurizer in operation	Return to 2 vessel operation.
Date of Run	10/19, 20, 23/72	10/25/72	10/26/72
Run Duration with H_2S Feed, hours	42.7	1.5	11.6
Purpose of Run	Repeat A15 increasing regenerator from 35 to 75 minutes residence time	Examine change in refractory CaS as acceptor was held at gas desulfurizer conditions	Repeat A4, but with no air in regenerator. Examine effect of H_2O/CO_2
Feedstock	28 x 35 Canaan dolomite	28 x 35 Canaan dolomite	35 x 48 Tymochtee dolomite
Shutdowns	Voluntary	Voluntary	Loss of inventory due to attrition
Results and Conclusions	1. No effect of increased residence time in regenerator.	1. No change in refractory CaS when held at gas desulfurizer conditions.	1. Hardening due to transient liquid formation did not occur in A4. 2. Change in H_2O/CO_2 ratio in regenerator between .5 and 1.7 had no discernible effect.

Run Number	A19
Unit Revisions	None
Date of Run	10/26, 27/72
Run Duration with H_2S Feed, hours	14.8
Purpose of Run	Repeat A12 but with gas desulfurizer at 1650°F
Feedstock	28 x 35 Buchanan dolomite
Shutdowns	10/27 Plug in H_2S feed line. 10/27 Loss of inventory due to attrition.
Results and Conclusions	1. No change in attrition or other results due to 1650°F operation.

Table 28

Summary of Gasifier Demonstration Runs

Run Number	D11	D12-A	D12-B
Unit Configuration	Figure 17	No change	No change
Data of Run	11/17/72	11/20/72	11/20/72
Run Duration, hours	12	2	5
Purpose of Run	Demonstrate operability at simulated conditions at point of entry in gasifier		
Temperature, °F	1725	1775	1775
Feedstock	←Char made from Pittsburgh Seam coal pretreated at 1200°F (Loveridge coal)→		
Shutdowns	Voluntary	Heating element broke in steam generator.	Transfer line plugged.
Results and Conclusions	1. No ash slagging. 2. Process operable.		

Run Number	D12-C	D12-D	D12-E	D13
Unit Configuration	No change	Feed line from bottom	No change	No change
Data of Run	11/28/72	11/28-29/72	11/30/72	12/18/72
Run Duration, hours	4	8	4.5	6.2
Purpose of Run	←Demonstrate operability at simulated conditions at point of entry of gasifier →			
Temperature, °F	1775	1775	1775	1775
Feedstock	← 1200°F Loveridge Char →			1200°F Loveridge char pretreated at 1400°F
Shutdowns	Transfer line plugged	Transfer line plugged	← High ΔP and ΔT in vessel →	
Results and Conclusions	1. Coke like material in vessel.		←1. Deposit at bottom of vessel →	

Table 29

Summary of Gasification Kinetics Runs

Run Number	K1-K7	K2-A-K7-A
Unit Configuration	Figure 18	No Change
Date of Runs	12/5-12/72	12/12-15/72
Run Duration, hours	102	71
Purpose of Run	Study influence of gaseous components on the rate of gasification at 30% char burnoff	Study influence of gaseous components on the rate of gasification at 60% char burnof
Temperature, °F	1620	1620
Feedstock	Char from Loveridge coal pretreated at 1600°F	Combined K1-K7 Product
Results and Conclusions	1. Gasification kinetics data on char from Pittsburgh Seam coal were obtained at 30% char burnoff.	1. Gasification kinetics data on char fro Pittsburgh seam coal were obtained at 60% char burnoff.

Run Number	K10-K16	K11-A-K16-A
Unit Configuration	Char inlet line through bottom of the vessel	No change
Date of Run	1/2-9/73	1/10-17/73
Run Duration, hours	102.5	74.5
Purpose of Run	Study influence of gaseous components on the rate of gasification at 30% char burnoff.	Study influence of gaseous components on t rate of gasification at 60% char burnoff.
Temperature, °F	1700	1700
Feedstock	Char from Loveridge coal pretreated at 1600°F	Combined K10-K16 Product
Results and Conclusions	1. Gasification kinetics data on char from Pittsburgh seam coal were obtained at 30% char burnoff.	1. Gasification kinetics data on char were obtained at 60% burnoff.

Table 30

Summary of Liquid-Phase Claus Reaction Operations

Run Number	C1	C2	C3
Unit Revisions		Enlarged the Condensate Receiver	None
Date of Run	12/13/72	12/15/72	12/21/72
Run Duration, hours	2.4	2.6	4.1
Purpose of Run	First exploratory run, 320°F	Repeat C1, get data for sulfur balance	See if 310°F operation improves sulfur collection
Liquid Feed		6% SO_2 in H_2O	
Results and Conclusions	1. Reaction goes readily. 2. Little soluble sulfur in product liquor. 3. Difficulty in removing product as Wackenroder's solution in the condensate.	1. About 40% conversion to elemental sulfur. 2. Sulfur collection still difficult.	1. About 42% conversion. 2. Sulfur collection O.K., probably due to large change in sulfur viscosity, 320-310°F.

Run Number	C4	C5	C6
Unit Revisions	None	Additional gas rotameter brought onstream	None
Date of Run	1/5/73	1/15/73	1/19/73
Run Duration, hours	6.5	2.5	7.9
Purpose of Run	Increase liquid flow fourfold to increase holdup in column.	Examine effect of thiosulfate addition to feed.	Study recycle of liquid feed.
Liquid Feed	1.68% SO_2 in H_2O	10% $Na_2S_2O_3$ in H_2O	Recycle liquor
Results and Conclusions	1. Very slight increase in conversion over C3.	1. About 35% of thiosulfate decomposed. 2. Conversion of feed gases to sulfur was 62%.	1. 67% conversion to elemental sulfur. 2. No buildup of acidity, or sulfur compounds in product liquor. 3. Conversion better than with once-through operation.

Run Number	C7	C8	C9
Unit Revisions	Packing reduced to 1/2 of column.	Packing reduced to 1/4 of column.	Packing removed. System repiped to allow gas to bubble through batch pool of liquid.
Date of Run	1/30/73	2/5/73	2/19/73
Run Duration, hours	6.2	6.7	5.5
Purpose	Examine effect of reducing packed reactor volume		Increase liquid volume by removing packing and bubbling gas through liquid.
Liquid Feed	Recycle Liquor		H_2O, one batch, no circulation.
Results and Conclusions	51.7% conversion. Conversion decreased.	43.1% conversion.	68.5% conversion in half full column was better than full packing column.

Run Number	C10	C11
Unit Revisions	None	None
Date of Run	2/23/73	3/8/73
Run Duration, hours	5.5	6.0
Purpose of Run	←Study effect of changing gas concentration→	
Liquid Feed	←H_2O, one batch, no circulation→	
Results and Conclusions	1. Conversion decreased.→ 2. System is between first and second order.→	

Table 21

Summary of Carbon Burnup Cell Operations

Run Number	CBC-1	CBC-2	CBC-3
Unit Configurations,	Figure 19	No change	No Change
Date of Run	1/25/73	1/29-31/73	2/1/73
Run Duration, hours	3	61	13
Purpose of Run	Explore the behavior of the carbon burnup cell	Is CBC operable at higher temperature	Explore the behavior of CBC at low bed expansions
Temperature, °F	1850	[illegible]	1850
Inert Bed Material	28 x 35 mesh dead burned dolomite	35 x 48 mesh dead burned dolomite	28 x 35 mesh dead burned dolomite
Feedstock	D-11 Product	Combined K2A-K7A Product	Combined K2A-K7A Product
Shutdowns	Large temperature gradient between bottom and top of bed	Slag formed at the bottom of reactor, sudden increase in bed temperature at the bottom	Deposit in steam generator
Results and Conclusions	1. Low bed expansion gives poor mixing and heat transfer. 2. Ash slagging is not a problem. 3. 100% burnoff of carbon in char.	1. Dead burned dolomite picks up sulfur, fluidizing characteristics of bed changed. 2. Ash slagging.	1. Run operable even with big spread of temperature. 2. No ash slagging.

Run Number	CBC-4	CBC-5	CBC-6
Unit Configurations,	No change	No Change	No change
Date of Run	2/5-7/73	2/8, 9/73	2/12-13/73
Run Duration, hours	13	12.5	9
Purpose of Run	Operation at higher bed expansion	Operability of combustion at different temperature levels	Run at 1900°F
Temperature, °F	1850	1750-1850	1900
Inert Bed Material	35 x 48 mesh dead burned dolomite	28 x 35 mesh silica sand	28 x 48 mesh silica sand
Feedstock	Combined K2A-K7A Product	D-12 Product	D-12 Product
Shutdowns	Voluntary	Voluntary	Water in supply air (rotameter ball stuck)
Results and Conclusions	1. Good operability. 2. Good mixing of bed. 3. Low temperature spread. 4. No ash slagging.	1. Good operability in broad range of temperatures. 2. No ash slagging.	1. Good operability in CBC combustion. 2. No ash slagging.

Run Number	CBC-7	CBC-8
Unit Configurations,	No change	No change
Date of Run	2/14/73	2/15-2/16/73
Run Duration, hours	5	26.5
Purpose of Run	Same as CBC-6	Demonstrate operability in a long run at high temperature
Temperature, °F	1900	1900
Inert Bed Material	35 x 65 silica sand	28 x 65 mesh silica sand
Feedstock	D-12 Product	D-12 Product
Shutdowns	Water in supply air	Voluntary
Results and Conclusions	1. Good operability in CBC combustion. 2. No ash slagging.	1. Operability proved. 2. No ash slagging.

VIII. PRETREATMENT STUDIES

A. Introduction

Eastern steam coals become fluid when heated through the temperature range of roughly 700-850°F and, therefore, require pretreatment to prevent caking at gasification conditions. Prior to the present EPA contract work, considerable background experience had been developed at Consol Research on pretreatment of highly-fluid Pittsburgh Seam coals for subsequent fluid bed processing at atmospheric pressure, i.e., for either low-temperature carbonization or gasification.

The work carried out under the first year of Contract No. EHSD 71-15(1) led to the following major conclusions relative to previous work on this subject:

1. Pretreatment under elevated pressure was less effective and the pretreatment operation was subjected to more severe operability restraints than the corresponding operation at atmospheric pressure.

2. A higher severity of pretreatment is required to establish operability during gasification at elevated pressure.

3. The severity of pretreatment required to establish operability increases with increasing particle size. This effect is somewhat unfortunate in that economic considerations favor use of a relatively coarse coal feed size consist.

Conditions were established in the limited amount of work carried out wherein operability was obtained in the pressurized pretreatment-gasification of high-sulfur Pittsburgh Seam coals. But the amount of preoxidation demonstrated was in excess of that imposed by the adiabatic restraints on the process.

Illinois No. 6 coals, however, were found to be operable in the pressurized pretreatment-gasification system within the adiabatic restraints of the process. LTC chars are likewise satisfactory feedstocks for the process, and these may be produced from Pittsburgh Seam coals by available processes, such as the Consol LTC process or the Lurgi flash carbonization process.

In the intervening period between expiration of the first year of the contract and its extension, additional process review as well as experimental work on the pretreatment problem were carried out at Consol Research. This work confirmed and extended earlier conclusions on the pretreatment problem as outlined below. These conclusions refer to the main objectives of the pretreatment work, i.e., to produce a relatively coarse high-density product, within the adiabatic restraints of the process, which is an operable feed to the gasifier.

1. Pretreatment is most effective at a given level of preoxidation when the amount of devolatilization accompanying it is maximized. Increased temperature is most effective in this regard but also increased residence time is important. Operability limitations in the pretreater itself determine the maximum level of devolatilization that can be achieved concurrent with preoxidation. Increased pretreater temperature also has an adverse effect in that it causes a decrease in particle density.

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2. Operability in the pretreater is improved when the oxygen partial pressure to which the coal is exposed is increased. The above holds true at a constant feed ratio of oxygen to coal. Another favorable effect of increased oxygen partial pressure is an increase in particle density of the pretreated product.

3. Improved operability is experienced in a high temperature pretreater if the coal is injected into a fluidized bed of inert solids. This maximizes preoxidation of the feed coal and minimizes competition for the input oxygen by the partially devolatilized coal.

4. Operability is improved in a high temperature pretreater by premixing or "precoating" of the coal feed with fine char or other inert solids.

5. Multistage pretreatment with increasing temperature between stages minimizes the required level of preoxidation to produce an operable gasifier feedstock and also maximizes the particle density of the pretreated product.

6. Improved operability in a high temperature pretreater is obtained by use of the draft tube principle. In the limit the pretreater becomes in effect an air-blown carbonizer.

The last conclusion is derived from a review of experience obtained in the pilot plant carbonizer operated as part of the CSF Process at Cresap, West Virginia,(14) which showed that improved operability in the pretreatment step could be achieved by incorporating the concept of a draft tube. The coal feed enters into the draft tube where it is mixed with a very high rate of circulating inert bed solids, i.e., char. The Cresap experience shows that this technique causes a significant improvement in operability in the handling of highly caking feedstocks. Thus, it was anticipated that higher temperature operation with more thorough decaking of the coal with a limited extent of preoxidation would be possible.

Two pretreatment processing techniques incorporating the draft tube concept were investigated. A schematic diagram of the first process is shown in Figure 28. Dilution, in the draft tube, of the incoming raw coal by a large amount of decaked coal from the external bed was to allow the temperature of preoxidation to be raised sufficiently to decake the coal.

The initial preoxidation reactions occur in the draft tube where the inlet oxygen partial pressure is 3.15 atm at 15 atm system pressure. Any oxygen not consumed in the draft tube is reacted in the external bed above the tube. The external bed supplies additional residence time to allow further devolatilization which completes the decaking of the coal. The bed is fluidized at a low superficial velocity with a small fraction of the total air required for adiabatic preoxidation.

A variation on this method is to preoxidize in two stages with injection of previously oxidized coal into the draft tube of the second stage.

The principle of the preoxidation method of pretreatment is to convert the coal to a more rigid structure via oxidation such that the fluidity is severely reduced when the coal undergoes pyrolysis. The Seeded Coal Process shown in Figure 29 operates on just the reverse principle and actually utilizes the natural fluidity of the coal. In the process visualized, char would be circulated at a high rate by means of lift gas through a draft tube immersed in a normal fluidized

Figure 28

PREOXIDIZED COAL VIA DRAFT TUBE

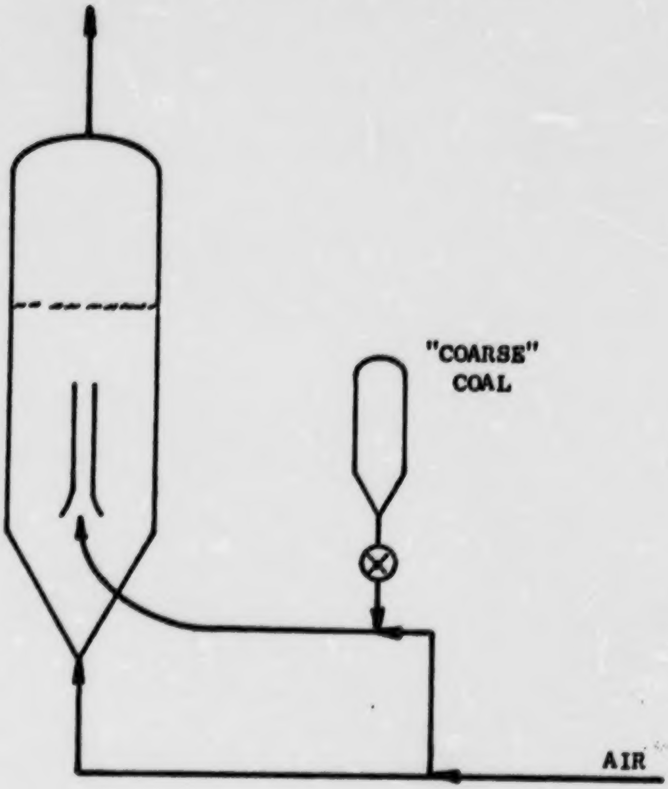
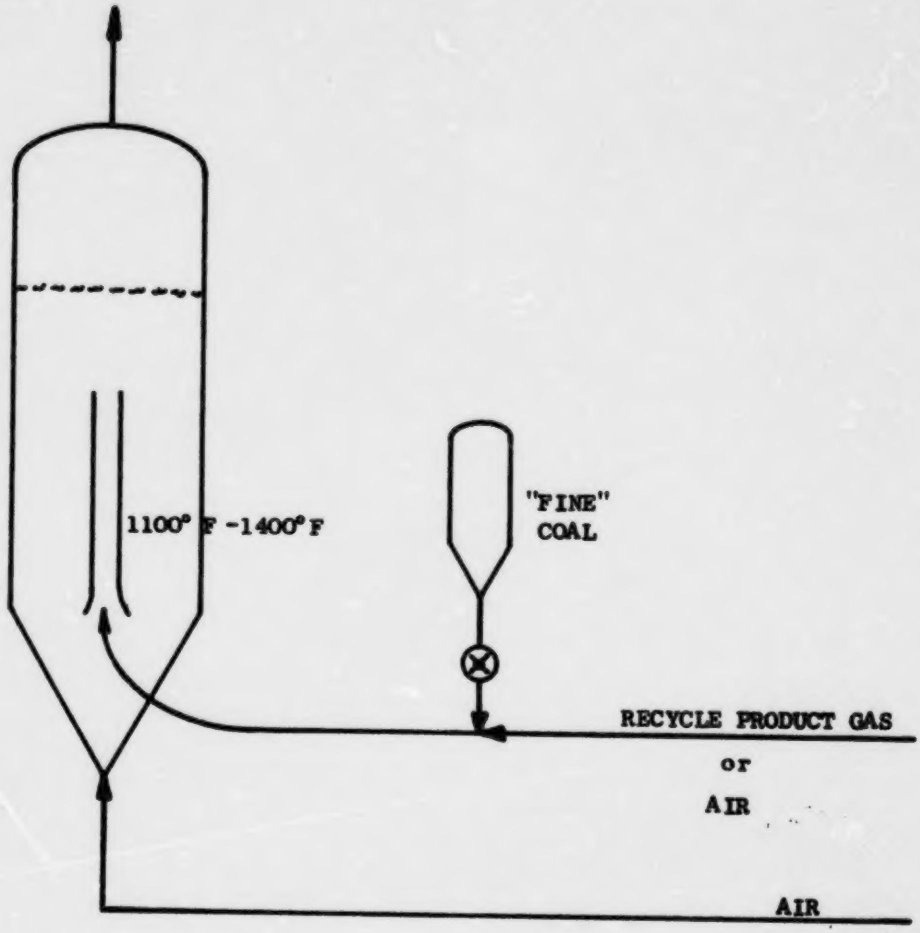

"COARSE"
COAL
AIR

Figure 29

SEEDED COAL PROCESS


1100° F -1400° F
"FINE"
COAL
RECYCLE PRODUCT GAS
or
AIR
AIR

bed. Coal and fine seed char would be fed into the draft tube. The external fluidized bed would be maintained at 1000-1400°F, either by injection of air or hot fluidizing gas from the gasification step. The coal melts, smears out over the surfaces of the seed char and external bed material and then solidifies on the completion of pyrolysis.

B. Draft Tube Studies

The pretreater-preoxidizer vessel (Section IV-C) was modified by installation of a draft tube to promote internal mixing of the fluidized bed and, therefore, increase operability. Schematic diagrams of the four draft tube configurations which were tried are shown in Figures 30 and 31 along with some pertinent dimensions.

The same model(2) used to predict the performance of a vertical pneumatic transfer line can be applied to a draft tube immersed in a fluidized bed. The pressure gradient across the fluidized bed external to the draft tube supplies the driving force to move the bed particles and feed particles through the tube.

Batch beds of precarbonized char were used at 15 atm system pressure. Normally, all gas flows were N_2. Suitable pressure taps were provided to measure the density of the external bed and the ΔP across the draft tube. Thermocouples measured the temperature of the material in the top end of the draft tube and of the external bed.

With the vessel as shown in Configuration A (Figure 30), 28 x 100 mesh char was used in the external bed at 900°F. The solids flow rate through the tube was determined by periodically feeding char at room temperature and at known rates into the draft tube. From the measured decrease in temperature of the material in the top of the tube, the solids rates were calculated by heat balance. Results showed flow rates in the range of 500-900 lb/hr. Using the measured ΔP's across the tube, calculations involving the pneumatic transfer line model showed that, to achieve solids flow rates as high as were indicated by the heat balances (460,000-840,000 lb/hr-ft^2 of draft tube cross section), some of the fluidizing gas from the external bed must have entered the tube, along with the solids.

In Configuration B, with a larger diameter draft tube, no quantitative measurements were made. However, qualitative checks by feeding cold char showed that the solids throughput was in excess of 1000 lb/hr.

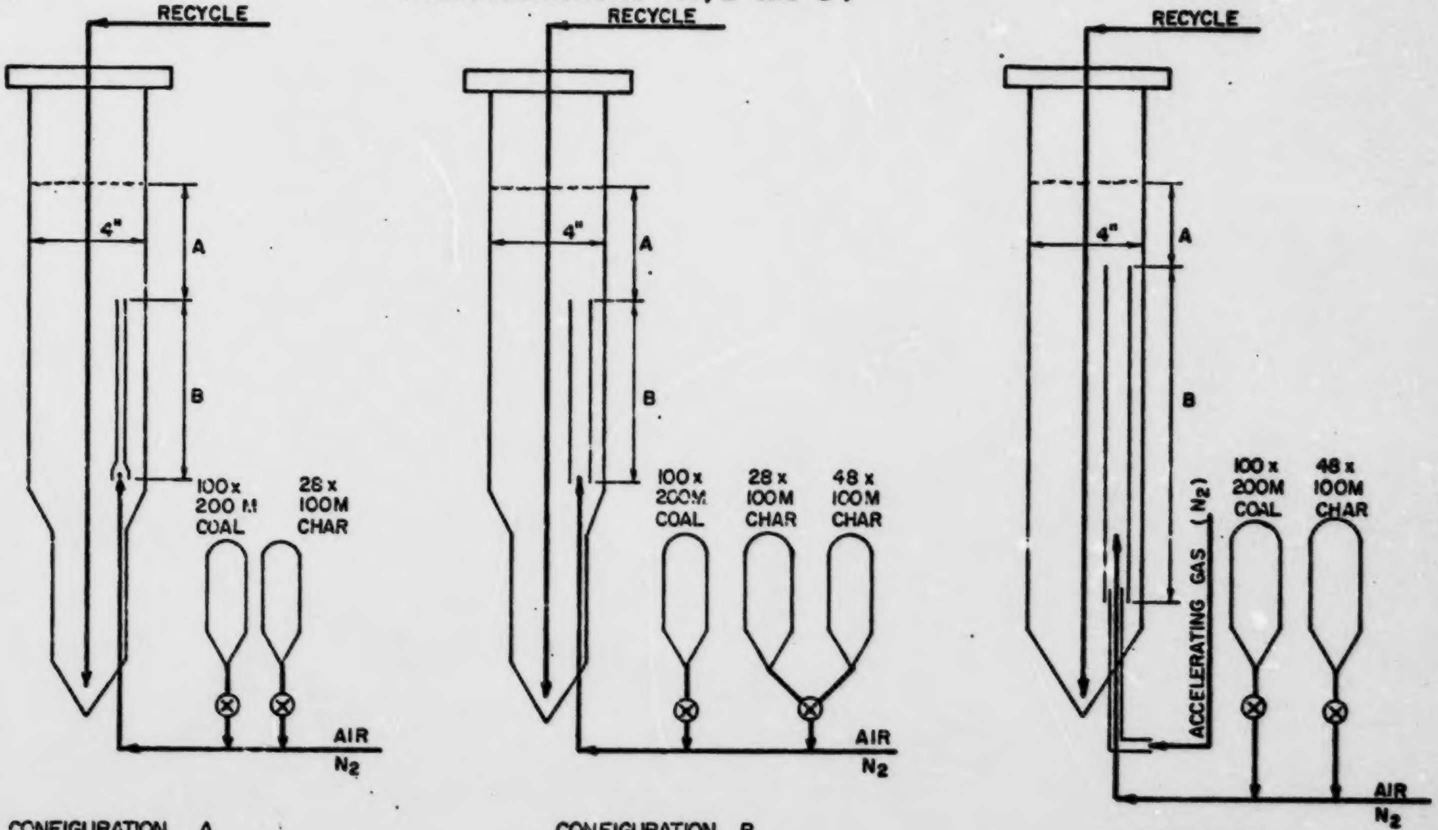
In Configuration C, a different measurement technique was used. The external bed was 48 x 100 mesh char, operated at 1500°F and 15 atm. system pressure. At this higher temperature it was shown that all oxygen was consumed when air was fed to the draft tube. By means of bed ΔP measurements the bed level was dropped below the weir to a level corresponding to the top of the draft tube. Then, air was substituted, mol for mol, for some of the nitrogen entering the solids feed line. From the measured temperature rise of the material in the top of the tube, the solids flow rate was calculated as 1500 lb/hr by heat balance.

Data obtained with Configuration C showed that most of the fluidizing gas fed to the external bed had passed through the draft tube. Also, particle Reynolds numbers inside the draft tube were barely above the Stokes Law range, a situation not conducive to good mixing. Configuration D (shown in Figure 31) was obtained by modifying Configuration C as follows: To allow installation of an external

FIGURE 30

CONFIGURATION OF DRAFT TUBES USED IN DRAFT TUBE AND SEEDED COAL TESTS

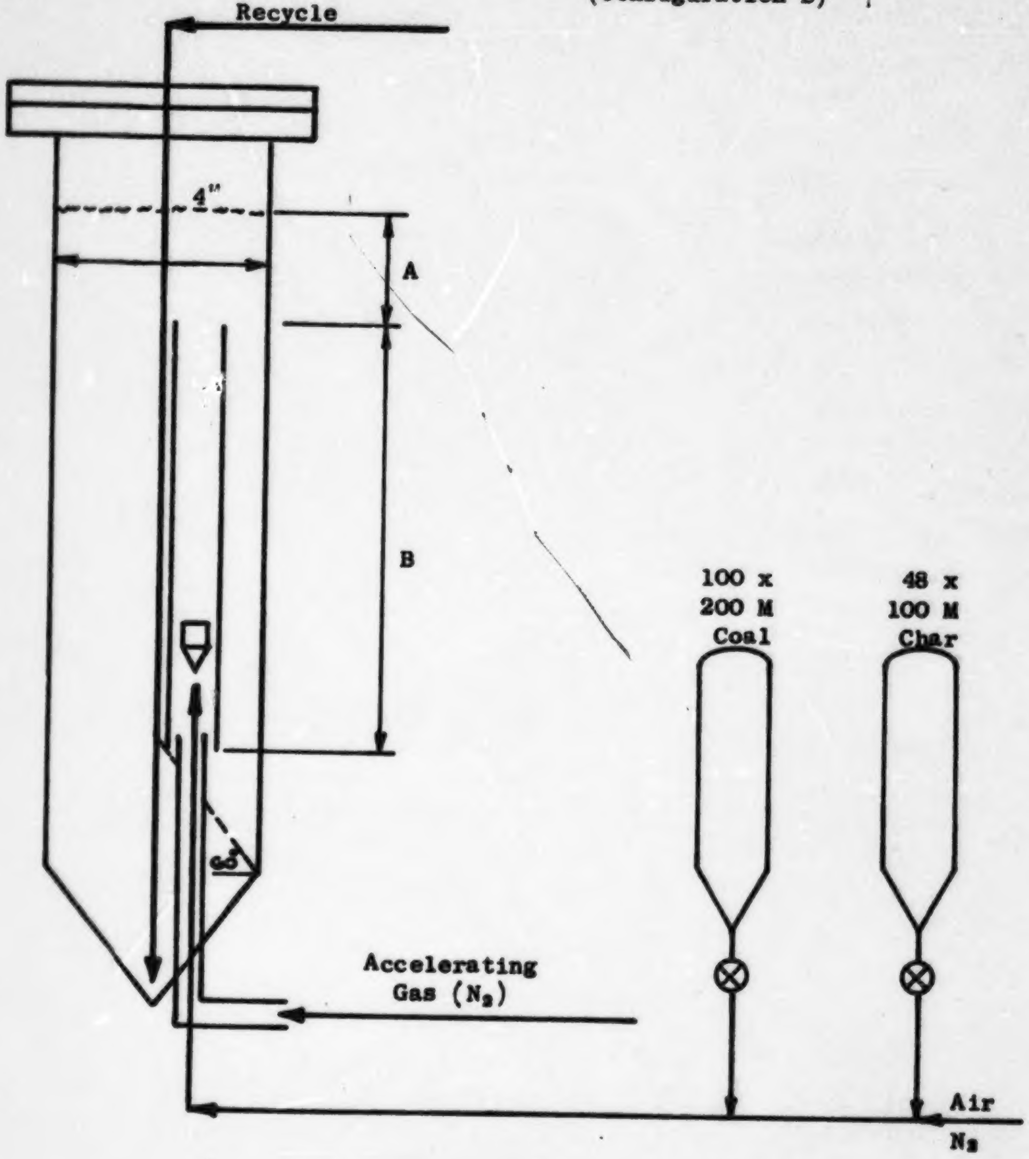
(CONFIGURATIONS A, B and C)


RECYCLE
4"
A
B
100 x 200 M COAL
28 x 100M CHAR
AIR
N2
RECYCLE
4"
A
B
100 x 200M COAL
28 x 100M CHAR
48 x 100M CHAR
AIR
N2
RECYCLE
4"
A
B
ACCELERATING GAS (N2)
100 x 200M COAL
48 x 100M CHAR
AIR
N2

	CONFIGURATION A	CONFIGURATION B	CONFIGURATION C
Dimension A	8"	8"	6"
Dimension B	24"	24"	34"
Draft Tube	.500"O.D. x .444" I.D.	.750"O.D. x .680" I.D.	.750"O.D. x .680" I.D.
Coal Feed Line	.250"O.D. x .180" I.D. tip positioned halfway into skirt	.250"O.D. x .180" I.D. tip positioned 1 inch above bottom of tube	.250"O.D. x .180" I.D. tip positioned 5 inches above bottom of tube
Accelerating Gas Line	—	—	.375"O.D. x .305" I.D. tip positioned 1 inch above bottom of tube

Figure 31

Configuration of Draft Tube Used in Seeded Coal Tests
(Configuration D)


Recycle
4"
A
B
60°
Accelerating
Gas (N_2)
100 x
200 M
Coal
48 x
100 M
Char
Air
N_2

CONFIGURATION D

Dimension A	4"
Dimension B	34"
Draft Tube	.750" O.D. x .680" I.D.
Coal Feed Line	.250" O.D. x .180" I.D. Tip positioned 5-inches above bottom of tube
Accelerating Gas Line	.375" O.D. x .305" I.D. Tip positioned 1-inch above bottom of tube
External Baffle	3-5/8" x 1-3/4" Elliptical, 60° from the horizontal
Internal Baffle	3/8" D x 60° Cone Tip positioned 1/2-inch above coal feed line

baffle, which would maintain fluidization of the external bed, the draft tube was raised two inches and the inlet lines were lengthened accordingly. An elliptical baffle 3-5/8" x 1-3/4" x 1/16" thick was welded to the accelerating gas line below the mouth of the tube at a slope of 60° from the horizontal. To help promote mixing, a conical baffle was installed inside the tube with the apex of the cone positioned one-half inch above the end of the coal inlet tube.

Tests with an inert bed of 48 x 100 mesh char at 1500°F and 15 atm. system pressure showed that the external baffle was effective. The solids circulation rate upward through the tube was measured as before by substituting a known amount of air for some of the nitrogen entering the solids feed line. From the measured temperature rise, the solids flow rate was calculated as 900 lb/hr by heat balance. Calculations involving the pneumatic transfer line model showed that without the external baffle about 270 of the 340 SCFH of nitrogen fed to the bottom of the external bed had entered the draft tube, whereas with the baffle, the flow was reduced to about 60 SCFH. This 60 SCFH corresponds closely to the void volume associated with 900 lb/hr of solids at the fluidizing conditions which existed in the external bed.

C. Pretreatment Using the Seeded Coal Process

In the Seeded Coal Process, finely sized coal and seed char are fed to a draft tube. The external bed of decaked material is maintained in the temperature range of 1000-1400°F by reaction with air. The coal melts, smears out over the surfaces of the seed char and external bed material, and then solidifies on completion of pyrolysis.

Thirty-one exploratory tests of the concept of the Seeded Coal Process were completed. Summarized conditions and results are shown in Table 32. Ireland Mine coal, sized to 100 x 200 mesh, was used. Detailed discussion of the results of individual runs will not be given because, as will be shown below, the general level of operability was severely hindered. While moderate agglomeration may be tolerable in a process vessel, the clearances in our draft tube were such that even small agglomerates were sufficient to jam up the draft tube.

Except in the tests where overt plugs occurred, as noted in Table 32, all the product material which overflowed the weir contained various ammounts of agglomerates. Agglomerates were recovered from the product material by screening. No agglomerates larger than 10 mesh were found. Microscopic examination of the product at 30 magnification showed that smearing of the melted coal occurred roughly in inverse proportion to the amount of agglomerates which had formed. The smeared coal material was readily apparent since it has a higher reflectivity than does the surface of the precarbonized char used in the external bed, and as seed material.

Nonuniform smearing showed itself by the presence of agglomerated external bed particles cemented together by bridges of fresh coal material. In some tests, the bridges were absent but agglomerates had been formed by film-to-film contact of the fresh coal material.

The evolution of the reactor configuration was as follows:

The first draft tube was installed in the "boot" reactor used in our 1971 work. The coal feed line was placed halfway up into the draft tube skirt which was 0.75" O.D. (Configuration A, Figure 30). The results of the preoxidation run described later, and Tests 1 through 5 (Table 32) showed that a possible cause

Table 32

Summary of Conditions and Results for Seeded Coal Tests
Ireland Mine Coal (100 x 200 Mesh)

Fluidizing Velocity: 0.30 ft/sec at top of external bed

Test No.	Draft Tube(1) Configuration	°F	Size, Tyler Mesh		Feed Rate, lb/hr		Percent of Adiabatic Preoxidation Level(2)	Duration of Coal Feeding, Minutes	Gas Flow to Coal Feed Line, SCFH	Gas Flow to Accelerating Section, SCFH	Comments(3)	Test No.
			Bed Char	Seed Char	Coal	Seed Char						
1	A	1200	28 x 100	28 x 100	2.0	0	48	3.3	60	0		1
2		1300			2.0	0	220					2
3		1300			2.0	5	220				Fewer agglomerates than in Test 2	3
4		1400			2.0	5	220					4
5		1400			1.5	15	220				Fewer agglomerates than in Test 4	5
6	B	1225		(4)	2.0	0	100	3.3	150			6
7		1225					0	3.3				7
8		1225					0	6.5			Mouth of tube choked with agglomerates	8
9		1300					100	3.3				9
10		1400						0.7			Mouth of tube choked with agglomerates	10
11		1100						3.3				11
12		1200						3.3				12
13		1300						3.3				13
14		1400						2.5			Mouth of tube choked with agglomerates. Repeat of Test 10	14
15		1200						3.3				15
16		1250		28 x 100		3		3.3			Fewer agglomerates than in Test 15	16
17		1250						9.0				17
18		1400						3.3			Fewest agglomerates of all tests through 18	18
19		1500						~ 1.0			Caked in coal feed line	19
20	C	1000	48 x 100					3.3	54	96		20
21		1000							53	57		21
22		1000							37	113		22
23		1500							72	78	Caked inside draft tube	23
24	D	900		(4)		0			85	85	Little or no smearing	24
25		1000										25
26		1100										26
27		1200										27
28		1300									Fewest agglomerates of all tests	28
29		1400										29
30		1500									Caked in draft tube	30
31		1300	-100	-100		4		3.5			24 M maximum agglomerate size	31

(1) See Figures 30 and 31.
(2) See Figure 32 for adiabatic preoxidation level at given bed temperature.
(3) Agglomerates formed in all tests but no plugs occurred except when coal caked in the draft tube.
(4) Seed char was not fed.

of inoperability was very poor mixing of the feed coal and external bed material in the skirt of the tube. Test 5, where the feed coal was premixed with ten parts of inert seed char, produced fewer agglomerates than in any of the previous runs.

In Configuration B, the diameter of the draft tube was increased to allow the coal feed line to be positioned inside the tube. No marked improvement in operability was noted. In some of the tests, as noted in Table 32, the mouth of the tube became choked with agglomerates which entered the tube from the external bed. The radial clearance between the coal feed line and the wall of the draft tube was about 0.22 inch. Very few agglomerates (say 10 x 14 mesh) would be required to bridge the opening.

For Configuration C, a new vessel was made. Elimination of the reactor boot allowed a longer draft tube to be installed. To improve internal mixing, a separate gas stream was fed into the mouth of the tube in order to accelerate the external bed particles. The coal was fed through a concentric line whose tip was positioned five inches above the mouth of the draft tube, as shown in Figure 30. To decrease the sensitivity toward choking by any agglomerates which may form, the size consist of the external bed of char was decreased to 48 x 100 mesh. Only two temperatures, representing the extremes at which the Seeded Coal Process was expected to be operable, were used with this vessel configuration. Agglomerates were recovered by screening at 20 and 48 mesh. No agglomerates larger than 20 mesh were found.

In most of the tests, air was fed to the draft tube along with the coal. In principle, the Seeded Coal Process does not require prior preoxidation of the coal, although this may be desirable in order to alter the fluidity characteristics of the melted coal. Since the retention time of the particles in the tube was very short (about one-half second), air was used during the experiments primarily to aid in bringing the feed coal particles to the bed temperatures quickly.

Figure 32 shows the amount of preoxidation, with adiabatic constraint, required as a function of temperature, the level of preoxidation being defined by: percent preoxidation = 100 (lb O_2 reacted/lb dry feed coal). The basis for the calculations are shown on the plot.

After Test 23 was completed, the test data (Draft Tube Studies) obtained with the Configuration C vessel were used in calculations involving the pneumatic transfer line model. Results showed that most of the fluidizing gas fed to the external bed had passed through the draft tube. Thus, the external bed in Tests 6 through 23 was a moving, fixed bed, an ideal climate for agglomerate formation from particles which had an incompletely solidified film of fresh coal material. The calculations also showed that the particle Reynolds numbers inside the draft tube were barely above the Stokes Law range, a situation not conducive to good mixing of the feed coal with the external bed material passing through the tube.

Appearance of the agglomerates collected showed that they were coal rich, i.e., incomplete mixing of the coal feed with the char bed solids had occurred. In Configuration D, an external baffle kept most of the fluidizing gas out of the draft tube, and an internal baffle was used to promote solids mixing in the draft tube.

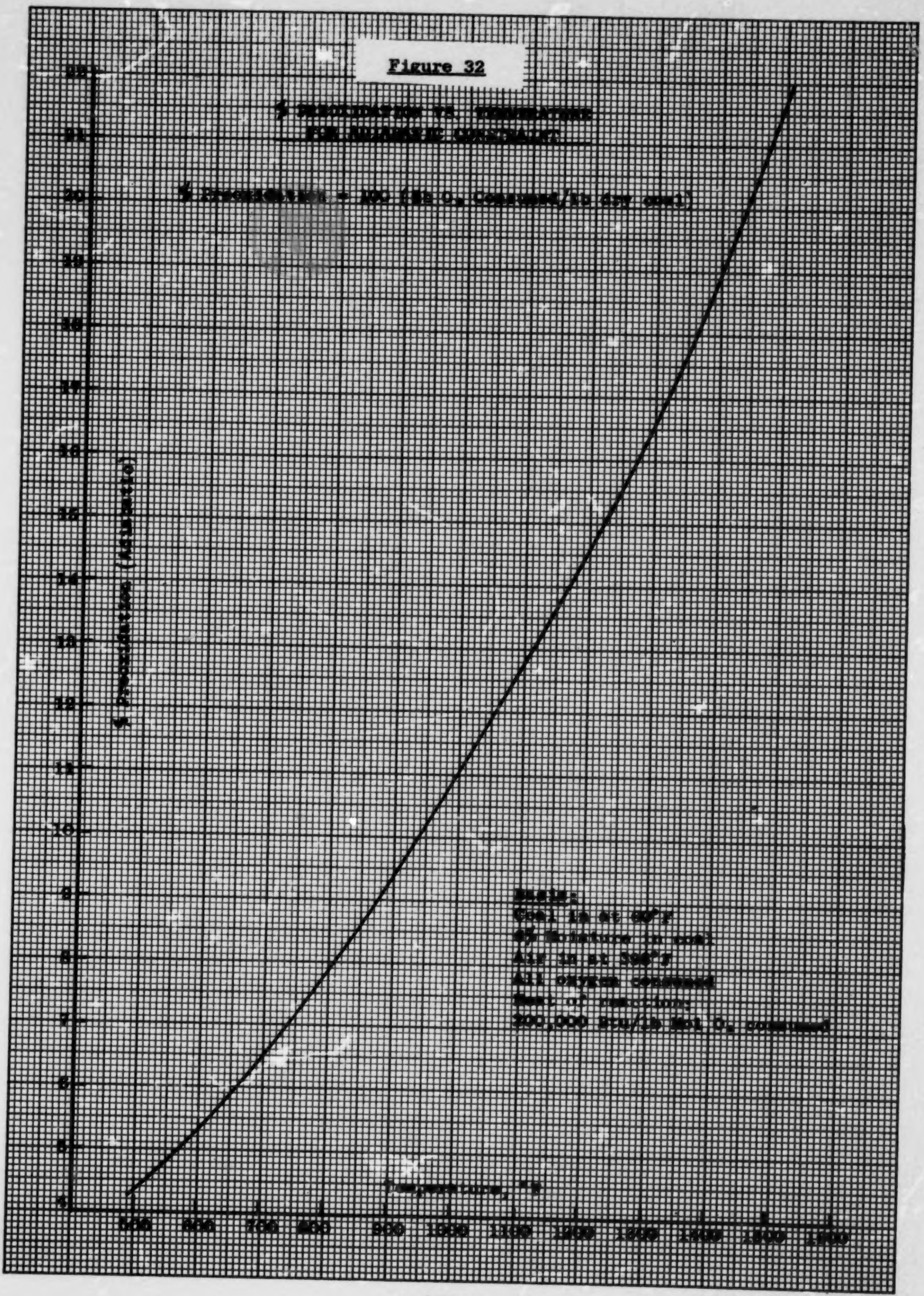


Figure 32

% PREOXIDATION VS. TEMPERATURE FOR ADIABATIC CONSTRAINT

K·E 10 X 10 TO ½ INCH 7 X 10 INCHES 46 1323 MADE IN U.S.A. KEUFFEL & ESSER CO.

Seven tests were made with the Configuration D draft tube, using an external bed of 48 x 100 mesh char at 15 atm. system pressure. Conditions for the runs are given in Table 32. Tests were made at temperatures from 900 to 1500°F, in 100° increments. Temperature limits of operability were established as follows: (1) at 900°F little or no smearing occurs as was shown by presence of coal-derived material in the form of hollow spheres in the bed after the run, and (2) at 1500°F caking occurred in the draft tube.

The products from the runs at 1000 to 1400°F all showed more uniform smearing than in any of the previous runs without the internal baffle. At the end of each run, the system was depressured and the bed was drained by removing the coal inlet line. The hot bed material was quenched rapidly by contact with dry ice in the catchpot. The entire bed material then was screened at 28 and 48 mesh. A characteristic of all the run products was that all contained some +48 mesh agglomerates which were external bed particles cemented together by a thin film of coal-derived material. No agglomerates larger than 28 mesh were found. The fewest agglomerates occurred at 1300°F, indicating that this may be the optimum temperature with respect to uniformity of smearing. The amounts of +48 mesh agglomerates which formed are listed below:

Temperature, °F	+48 Mesh Agglomerates/Wt. % of Bed Inventory
1000	18.0
1100	16.0
1200	15.5
1300	8.0
1400	10.7

The particle density, measured in mercury, for the +48 mesh agglomerates formed at 1300°F had a high value of 85 lb/ft^3.

An attempt was made to run for a prolonged period at 1300°F and 15 atm. system pressure to determine the size distribution of the "equilibrium" product. To simulate the seed char in the commercial embodiment (fines from the internal cyclones in the gasifier) an initial external bed of -100 mesh precarbonized char was established. Then, 100 x 200 mesh Ireland Mine coal and additional -100 mesh char were fed to the draft tube at rates of 2 and 4 lb/hr, respectively. The fine char contained a considerable amount of -325 mesh material which was elutriated from the reactor. The outlet piping system of the present equipment was not designed to handle large amounts of solids. The run had to be terminated after 35 minutes of feeding coal because the outlet system began to plug. Thus, an equilibrium bed was not established. However, analysis of the bed showed that it contained 50 wt. % of +100 mesh agglomerates, with a top size of 24 mesh. This material had a high particle density of 82 lb/ft^3.

The high particle density achieved is favorable, in that "smearing" of liquid coal over the seed particles apparently is occurring as desired.

The small size of the existing equipment precludes any further meaningful studies of the Seeded Coal Process. The radial clearance between the inlet line and the wall of the draft tube is only 0.15 inch. The mouth of the tube eventually would become choked by the larger agglomerates which inevitably would be formed.

D. Preoxidation of Ireland Mine Coal

The first draft tube (Configuration A) was sized to allow the use of 100% air (3.15 atm. P_{O_2}) as carrier gas to the draft tube, consistent with the maximum capacity of the overflow weir (16 lb/hr of preoxidized coal). At the conclusion of the draft tube tests, the bed temperature was decreased to 850°F and "coarse" Ireland Mine coal (24 x 100 M) was fed into the draft tube at conditions shown below:

Coal Feed Rate	16 lb/hr
Carrier Gas to Draft Tube, SCFH	
Air	62
Fluidizing Gas to Bottom of External Bed, SCFH	
Recycle	400
Air	15
N_2	110
Total Inlet Flow	587
% Preoxidation Equivalent to Air Fed	
In Draft Tube	6.9
In External Bed	1.7
Total	8.6

The total air flow corresponded to adiabatic preoxidation, 8.6% at 850°F (Figure 32). After ten minutes of coal feeding, the ΔP across the external bed increased sharply indicating that massive caking had occurred. On disassembly of the vessel, the bed contained large chunks of agglomerated material. The coal particles had cemented together the char particles present in the start-up bed.

A series of runs were then made in which a finer size consist, nominally 65 x 100 mesh, of the raw coal feed was used in conjunction with two stages of preoxidation. From prior work both expedients are in the direction of reducing the excessive preoxidation required in single stage treatment of relatively coarse coal.

a. First Stage - Run PR1 - The draft tube was removed from the reactor for this run. At the low temperature level of 675°F chosen for the run, the draft tube probably would give no benefit since the plastic range of the coal lies at higher temperatures and caking/agglomeration should not be a problem.

Programmed conditions called for the adiabatic level of 6.3% preoxidation. The actual coal feed rate was somewhat higher than the programmed value, with the result that 5.7% preoxidation was achieved. The run was completely operable and scheduled shutdown was made after making 143 pounds of steady-state product.

b. Second Stage at 775°F - Run PR1B - After steady-state conditions at 750°F had been reached in Run PR1A in which complete operability was demonstrated, the bed temperature was raised to 775°F for Run PR1B. The preoxidation level was increased purposefully to give a conservative total level for both stages of 11.3% preoxidation, which is 50% greater than the adiabatic level at 775°F. This run also was completely operable with no caking or agglomeration occurring.

The Run PR1 product and all the air were fed into the Configuration D draft tube. In a preoxidation run, the draft tube probably makes no intrinsic contribution to the process. In the tube, the incoming first-stage coal product and air are immediately diluted with a large amount of external bed material. The draft tube was used to assure a smooth transition from the start-up conditions involving an initial bed of inert char and to prevent localized hot spots caused by the highly exothermic preoxidation reactions. Axial traverses across the entire bed showed that the temperature was constant to within 4°F.

C. Second Stage Preoxidation Attempt at 800°F - In an effort to obtain a more highly devolatilized and, therefore, a more thoroughly decaked product, the bed temperature was raised to 800°F via the electrical heaters at the end of the material balance period of Run PR1B. After about one-half hour, the pressure drop across the bed had increased and a large temperature gradient had developed. Inspection of the reactor after shut down showed that it was full of large chunks of agglomerates.

Detailed results of Runs PR1 and PR1B are given in Tables 33 through 36. Inspections of the preoxidized coal product from Run PR1B show that the material was considerably swollen and had a particle density of 49 lb/ft^3, compared with the raw coal value of 82 lb/ft^3. This result was not anticipated because our 1971 work had indicated that the smaller size fractions of the preoxidized coal products had suffered relatively little swelling. Some comparisons are shown below with data from two runs made during the earlier work:

Run Number	1P	2P2	PR1B
Raw Coal Size Consist	←24 x 100 Mesh→		65 x 150 Mesh
Temperature, °F	700	750	775
Percent Preoxidation	19.5	18.6	11.3
Particle Density, lb/ft^3			
Mean of Entire Product	61.6	53.1	48.6
65 x 100 mesh Fraction	76.8	73.1	54.4

The lower density, 65 x 100 mesh, product produced in PR1B as compared with previous work may be due to the lower level of preoxidation and/or the higher temperature used.

The laboratory shock-heating test showed that the Run PR1B product would have been inoperable at gasifier conditions. The amount of agglomerates formed in the test was greater than for the Run 2P2 product which actually was fed to the gasifier at process conditions and which was shown to be inoperable.

E. Conclusions - Pretreatment of Ireland Mine Coal

The results of the exploratory studies strongly indicate that future studies of the Seeded Coal Process should be made with a larger reactor unit in which the draft tube diameter would be at least 2 inches (vs .680 inch at present). The potential advantages of the process are that it will supply a feedstock which assuredly is operable with respect to caking/agglomeration at gasifier conditions, and that it can produce a dense, closely sized feedstock substantially free of fines which will allow a higher gasifier throughput than was envisioned previously.

Table 33

Preoxidation Conditions and Results
System Pressure: 15 atm (206 psig)
Feed Coal Size Consist 48 x 150 Tyler Mesh
Ireland Mine Coal

Run Number	PR1 1st Stage	PR1B 2nd Stage
Temperature, °F	675	775
Inlet O_2 Partial Pressure, atm	.18	.40(1)
Fluidizing Velocity (top of bed), ft/sec	0.30	0.30
Moisture in Coal, Wt % as Fed	1.83	0.71
Input		
Coal Feed Rate, lb/hr (dry basis)	10.44	5.64
Lift Gas, SCFH		
Air	35	18.4
N_2	170	126
Fluidizing Gas, SCFH		
Recycle	417	417
N_2	0	0
Purges (N_2), SCFH to bed	5	5
Purges (N_2), SCFH above bed	7	11
Output		
Exit Gas Rate, SCFH (dry basis)	212	159
Exit Gas Composition, Mol % (dry basis)		
O_2	.14	<.01
CO_2	.76	.89
CO	.30	.44
CH_4	.09	.44
C_2H_6	.03	.10
C_2H_4	<.01	.01
C_3H_8	.02	.03
C_3H_6	<.01	.01
COS	.02	.03
SO_2	<.01	.01
N_2 (by difference)	98.64	98.04
Flow Rate, SCFH at top of bed	642	585
Water, lb/hr (corrected for coal moisture)		
Condensate	.677	.258
Moisture in Exit Gas	.008	.006
Tar, lb/hr	.106	.092
Preoxidized Coal, lb/hr	9.89	5.31
% Preoxidation(2)	5.71	5.67
Duration of Steady-State Period, hr	14.1	2.0
Total Product, ex. overhead fines, lb	143	10.4

(1) In draft tube.
(2) Lb O_2 consumed/100 lb dry feed to stage.

Table 34

Properties of Feed Coal and Products

Run Number	Ireland Mine Feed Coal		PR1		PR1A		PR1B	
			1st Stage		2nd Stage			
Temperature, °F	--		675		750		775	
Hydrogen, Wt % (dry basis)	4.87		4.64		3.52		3.52	
Carbon	69.88		70.37		70.44		70.60	
Nitrogen	1.25		1.08		1.24		1.35	
Oxygen (by diff.)	6.69		6.29		4.23		3.92	
Sulfur	4.65		4.60		4.55		4.52	
Ash	12.66		13.02		16.02		16.10	
Volatile Matter	41.3		35.5		24.2		23.8	
Size, Tyler Mesh	Wt %	Density	Wt %	Density	Wt %	Density	Wt %	Density
+28	--	--	--	--	0.5	--	0.6	--
28 x 35	--	--	--	--	1.8	--	6.6	44.3
35 x 48	--	--	0.7	--	10.2	49.7	14.8	39.0
48 x 65	16.1	--	27.4	62.0	42.9	46.7	34.5	46.4
65 x 100	71.3	--	67.3	69.6	40.0	51.5	38.1	54.4
100 x 150	11.4	--	4.4	76.7	4.0	53.2	4.5	56.9
-150	1.2	--	0.2	--	0.6	--	0.9	58.8
Mean Diameter, inches(2)	.00717		.00774		.00914		.00923	
Mean Particle Density, lb/ft^3(3)	82		67.6		50.5		48.6	

(1) Measured in mercury at 1 atm.
(2) Arithmetic mean.
(3) Reciprocal mean.

Table 35

Material Balances for Preoxidation

Basis: 100 lb Dry Feedstock

Run Number	PR1	PR1B	
Temperature, °F	675	775	
Preoxidized Coal	94.05	92.23	Output, lb.
Overhead Fines	.72	1.95	
Tar	1.01	1.63	
Carbon in CO + CO_2	.67	1.17	
Hydrogen in H_2O	.73	.52	
Hydrocarbons (C_1-C_3)	.17	.88	
Sulfur in SO_2 and COS	.03	.09	
Carbon and Sulfur in Condensate	.10	.10	
Coal Oxygen to Products	1.70	1.39	
Total	99.18	99.96	

Table 36

Distribution of Oxygen in Products of Preoxidation

Run Number	PR1		PR1B	
Temperature, °F	675		775	
	Lb/hr	Percent	Lb/hr	Percent
Output				
To Water				
Condensate	.602	76.7	.229	57.5
Moisture in Gas	.008	1.0	.006	1.5
To CO_2	.133	16.9	.118	29.5
To CO	.026	3.4	.029	7.3
To SO_2	0	0	.001	.3
To COS	.002	.2	.002	.5
In Tar	.002	.2	.013	3.4
Unreacted O_2	.012	1.6	0	0
Total	.785	100.0	.398	100.0
Input				
From Coal (by diff.)	.177		.078	
Lb/hr O_2 from Air	.068		.320	
Total	.785		.398	

Within the framework of an adiabatic preoxidation process, use of a fine size consist of the feed coal coupled with two stages of preoxidation cannot produce a feedstock which is operable in both the preoxidizer and gasifier. Such a process variation should reduce the total preoxidation required, but from the present work the magnitude of the reduction has not been demonstrated. It is clear, however, that the required total preoxidation level exceeds 11.3%. Conceivably, a three-stage adiabatic preoxidation with the third stage at 800°F+ in which inlet oxygen partial pressures higher than we are able to provide with the existing equipment would produce an operable feedstock with a lower level of preoxidation. However, the evidence obtained so far indicates that even in this process the product would have a small particle size and a low particle density which, in turn, would lead to a low gasifier throughput.

All of our work to date has shown that preoxidation at elevated pressure of the highly fluid coals such as Ireland Mine coal will always require a preoxidation level in excess of the adiabatic level.

IX. ACCEPTOR SULFUR CYCLE STUDIES

A. Introduction

The reaction,

$$CaCO_3 + H_2S = CaS + H_2O + CO_2,$$

is used for both gas desulfurization and acceptor regeneration. Conditions in the gas desulfurizer and regenerator are such that the equilibrium H_2S content of the cleaned fuel gas is low, and the equilibrium H_2S content of the regenerator offgas is relatively high.

Run conditions in this study generally simulated those used in the process design calculations, as given below:

	Gas Desulfurizing Reactor	Regenerator
Temperature, °F	1600	1300
Inlet Gas Composition, Mol %		
H_2	17	--
CO	18	--
CO_2	8	50
N_2	46	--
H_2S	ca. 1.0	--
H_2C	9	50
Acceptor Conversion, Mol % of Ca Converted	20	20

B. Cyclic Runs with Tymochtee Dolomite Feed

Runs A1-A4 and Run A18 were made using Tymochtee dolomite. Reactor conditions and results for the gas desulfurizer and regenerator are given in Tables 37 and 38, respectively. For Runs A1 and A2, producer gas was simulated by feeding H_2, CO_2, and H_2O, and making CO in the reactor by way of the water gas shift reaction,

$$H_2 + CO_2 = CO + H_2O.$$

For later runs, operations were simplified by also making all necessary steam via the shift reaction. Analysis of the exit gases and condensate showed that shift equilibrium was always attained.

Table 39 gives the analyses of the dry exit gases from both vessels. The CaS content of exit solids as a function of cycles is given in Table 40. As discussed earlier (Section V-E), a small fraction of the calcium in the stone reacts with impurities the first time it is heated. The numbers in Table 40 represent mols of CaS as a percentage of the calcium remaining after reaction with impurities in the stone is complete. Table 41 lists the size consist of the feed and of the last sample collected from the regenerator.

Table 37

Conditions and Results for Gas Desulfurizer With Tymochtee Dolomite Feed

System Pressure: 15 atm. (206 psig)
System Temperature: 1600°F

Run Number	A1	A2	A4	A18
Acceptor Size Consist, Tyler Mesh	28 x 35	28 x 35	35 x 48	35 x 48
Feed Rate, lb/hr (half calcined basis)	6.6	5.4	5.9	6.8
Solids Residence Time, minutes	32	39	35	33
Input, SCFH				
Recycle to Bed	350	260	130	133
H_2S	3.5	3.5	3.5	3.2
CO_2	40	51	35	35
H_2	53	53	48	48
H_2O	15	15	—	—
N_2	67	68	65	65
Purges (CO_2) to Bed	5	5	5	5
Purges (N_2) above Bed	15	15	15	15
Recycle Acceptor Lift Gas, above Bed	124 (once-through N_2)	158	92	71
Output in Cycle	1-3	1-3	1-3	2-3
Exit Gas Rate, SCFH (dry basis)	264	154	148	145
Composition, Mol %				
H_2	9.8	13.2	18.3	15 (a)
CO	10.2	20.4	17.3	19 (a)
CO_2	7.7	14.4	12.1	11 (a)
N_2	72.3	51.9	52.1	55 (a)
H_2S	.038	.075	.09	.088
Outlet Gas, Top of Bed				
Composition, Mol %				
H_2O	9.5	9.9	10.9	10
H_2	8.9	11.8	16.3	14
CO	9.2	18.4	15.4	18
CO_2	6.9	13.0	10.8	11
N_2	65.3	46.8	46.5	47
H_2S	.034	.068	.08	.0835
Flow Rate, SCFH, top of Bed	525	443	275	282
Fluidizing Velocity, ft/sec	.78	.66	.40	.42
Attrition, % of Feed Rate	2.5	18	5.6	4.9
Duration of Circulation with H_2S Feed, hr	6.1	2.6	7.1	11.6
Removal of Feed Sulfur, %	97	97	97	96
Removal of Feed plus Recycle Sulfur, %	93	92	94	93
% H_2S in Outlet/Equilibrium % H_2S	1.9	1.8	2.3	2.0
Conversion of Acceptor/Pass, mol %	21	36	23	19

(a) Estimate. Gas chromatograph recorder not functioning.

Table 38

Conditions and Results for Regenerator With Tymochtee Dolomite Feed

System Pressure: 15 atm. (206 psig)
System Temperature: 1300°F

Run Number	A1	A2	A4	A18 Phase 1	 Phase 2	 Phase 3
Solids Residence Time, min.	25	42	40	←	36	→
Input, SCFH						
H_2O	187	107	89	82	57	91
CO_2	188	108	82	82	107	53
Air	—	—	7.5	—	—	—
Purges (N_2) to Bed	10	10	10	←	8	→
Purges (N_2) above Bed	10	10	10	←	10	→
Purges (CO_2) above Bed	5	5	5	←	5	→
Output in Cycle	1-3	1-3	1-3	2	3	3
Exit Gas Rate, SCFH (dry basis)	214	133	110	105	130	76
Composition, Mol %						
CO_2	90.2	84.2	76.1	82	85	74
N_2	9.3	15.0	23.0	17	14	24
H_2S	.49	.83	.8	.885	.73	2.2
S_2	~ 0	~ 0	.08	~ 0	~ 0	~ 0
Outlet Gas, Top of Bed						
Composition, Mol %						
H_2O	46.6	47.6	43.5	47	33	59
CO_2	48.1	47.6	47.3	47	62	34
N_2	5.0	4.4	8.6	5	5	5
H_2S	.26	.49	.5	.54	.55	1.10
S_2	~ 0	~ 0	.03	~ 0	~ 0	~ 0
Flow Rate, SCFH, Top of Bed	388	279	186	171	172	152
Fluidizing Velocity, ft/sec	1.11	.80	.53	.48	.48	.43
Regeneration of Acceptor, Mol %	6.2	8.3	6.7	6.4	11.0	12.0

Table 29

H_2S Content of Exit Gases (dry basis)

Run No.	Gas Desulfurizer			Regenerator		
	Cycle No.	Mol % H_2S	% H_2S Removal	Cycle No.	Mol % H_2S	% Recovery of H_2S Fed to Desulfurizer
A1	.6	.037	97	1.1	.384	23.6
	1.7	.039	97	2.1	.492	20
A2	.6	.075	97	1.1	.621	22
A4	.5	.115	95	.7	.80	25
	1.6	.090	96	2.1	.82	28(1)
	2.6	.084	96.5	2.5	1.34	42(1)
A5	.9	>1.4	<8	1.2	.067	2
A6	2.0	.105	87	2.3	.262	29
	6.6	.144	82	4.5	.380	41
	9.1	.476	41	7.0	.411	45
	10.1	.511	37	9.6	.404	44
	11.8	.684	15	9.8	.354	39
				12.0	.367	40
A7	.3	.046	97	.5	.671	25
	1.4	.049	97	1.5	.927	35
	5.5	.048	97	5.7	1.39	53
	7.5	.058	96	7.8	1.69	64(1)
	8.6	.064	96	9.2	1.40	53(1)
	12.6	.672	59	12.5	1.90	72(1)
A8	—	.059	96	—	—	—
A9	—	.16	89	—	—	—
A11	—	—	—	1.5	1.41	54
A12	3.0	.122	93	1.7	2.01	76
	7.0	.094	94	2.4	1.68	64
				7.1	1.89	72
A13	0(2)	.123	93	2.2	2.14	83
	.9	.114	93	5.4	1.44	56
	5.3	.093	94			
A15	6.8	.207	87	4.1	1.45	64
	8.8	.817	50	7.0	1.41	62
	11.0	.99	40	8.8	1.41	62
	11.9	.93	43	11.0	1.35	59
	15.5	.645	61	11.9	1.20	53
				15.5	1.16	52
A16	.6	.046	95	.9	.283	24
	1.2	.071	92	1.2	.456	39
	2.4	.048	94	2.5	.456	39
	3.7	.048	94	3.8	.508	43
	5.2	.039	95	5.3	.464	39
	6.6	.047	94	6.6	.705	60
	6.8	.06	93	6.8	.58	49
	7.7	.132	84	7.7	.790	67
	8.5	.421	50	8.5	.445	38
	9.9	.645	23	10.1	.629	53
A18	1.6	.095	96	1.6	.885	29
	2.8	.088	96	2.8	.756	31
	3.3	.086	96	3.2	.703	29
	4.1	.081	97	4.1	2.27	54
				5.6	2.14	51
A19	2.5	.054	97	2.4	1.09	39
	4.9	.065	96	4.8	1.32	48
	7.0	.074	96	7.1	1.38	50

(1) The condensate contained ca. 3% of the feed sulfur as elemental sulfur.

(2) Taken during the presulfiding step.

Table 40

CaS Content of Exit Solids

Run No.	Gas Desulfurizer Cycle No.	Gas Desulfurizer Mol % CaS	Regenerator Cycle No.	Regenerator Mol % CaS
A1	.6	32.9	.5	16.7
	1.6	49.0	1.5	34.7
	2.3	60.6	2.15	49.6
A2	.5	32.1	.2	5.2
	.8	41.8	.5	11.8
	1.55	56.1	.7	15.9
			1.3	28.9
A4	.8	40.4	.4	25.8
	1.25	52.6	1.4	42.1
	1.8	58.9	2.4	52.9
	2.3	70.2	3.0	65.7
	2.9	81.1		
A5	ca. .9	1.1	ca. 1.2	0.9
A6	.5	15.3	.2	7.3
	.8	17.2	.7	14.5
	1.2	16.7	1.3	16.4
	1.6	20.1	2.0	17.2
	2.1	21.2	2.8	15.6
	3.6	24.1	3.3	23.5
	4.6	27.9	6.2	24.4
	12.6	42.0	9.0	25.5
	12.6 + 150 min.	49.9	10.4	26.0
			12.4	30.5
			12.6 + 150 min.	27.8
A7	2.5	33.5	.8	12.2
	6.0	66.7	3.4	32.0
	8.0	78.8	9.0	71.6
	11.3	96.8	12.9	85.3
	12.9	98.4	12.9 + 120 min.	75.9
	12.9 + 120 min.	98.4		
A8	—	85.6		
A9	—	94.8		
A11	2.0	32.6	1.5	15.7
	2.7	39.6	1.9	20.2
			2.3	23.8
			2.7	25.3
A12	1.2	26.4	.7	10.2
	2.1	33.9	4.2	31.5
	3.0	37.4	4.8	34.5
	4.0	42.4	7.2	44.9
	6.1	55.3		
	7.3	61.0		

*Includes ca. 4% $CaSO_4$

Table 40 (Cont'd.)

CaS Content of Exit Solids

Run No.	Gas Desulfurizer		Regenerator	
	Cycle No.	Mol % CaS	Cycle No.	Mol % CaS
A13	2.9	70.9	1.6	44.6
	4.1	72.7	3.9	64.0
	5.3	95.7	6.0	83.7
	6.4	88.5	8.3	88.6
	7.6	95.4	10.4	92.5
	8.8	97.6		
	10.0	98.8		
A15	4.6	77.2	.4	35.8
	8.6	96.6	1.9	37.5
	11.4	95.6	3.0	48.2
	13.0	96.3	4.1	62.2
	14.2	95.6	5.2	71.9
	17.2	96.4	8.3	88.6
			10.2	88.5
			12.1	88.6
			13.0	89.5
			14.8	89.3
			16.0	90.0
			17.0	89.9
A16	.7	23.3	.5	15.0
	3.2	59.7	3.0	49.0
	4.1	65.1	4.0	58.7
	6.8	94.2	6.8	81.9
	7.4	95.7	7.3	85.0
	8.5	96.2	8.5	87.7
	10.5	95.8	9.5	88.0
			10.5	88.3
A18	2.0	35.7	1.7	26.3
	3.3	52.5	3.2	40.9
	5.6	70.5	5.6	58.5
A19	3.5	43.2	3.6	39.0
	5.5	58.3	6.5	51.7
	7.2	72.8	7.2	57.6

Table 41

Size Consist of Acceptor Feeds and Products(1)

Data given on a weight % basis
Smallest size includes fines

Run Number	A1	A2	A4	A5	A6	A7	A8	A9	A11	A12	A13	A15	A16	A18	A19	
Size, Tyler Mesh	Product															**Size, Tyler Mesh**
20 x 28	4.7	6.1			61.4		3.2	4.9	1.0	6.7	13.6					20 x 28
28 x 35	84.1	70.5		33.0	29.2	30.0	48.4	48.2	39.9	35.6	76.4	37.8	36.4	2.0	23.9	28 x 35
35 x 48	9.7	15.1	61.8	62.5	7.5	38.6	40.1	41.8	20.3	25.7	8.9	36.8	32.1	70.8	19.1	35 x 48
48 x 65	1.4	8.3	23.0	4.3	1.9	31.4	8.2	5.1	38.8	17.2	1.1	25.4	31.5	14.2	22.2	48 x 65
65 x 100			6.4	0.1						14.8				13.0	34.8	65 x 100
-100			8.8	0.1												-100
Size, Tyler Mesh	Feed															**Size, Tyler Mesh**
20 x 28					61.0		3.1	3.1		17.3	15.0					20 x 28
28 x 35	100*	100*		15.8	29.6	42.1	48.3	48.3		70.7	80.1	91.0	91.0		100*	28 x 35
35 x 48			100*	84.2	6.3	41.2	46.6	46.6	100*	7.9	4.4	9.0	9.0	100*		35 x 48
48 x 65					1.5	9.9	2.1	2.1		4.1	0.4					48 x 65
65 x 100					1.4	6.8										65 x 100

(1) For once-through Runs A8 and A9 analyses are of stone exiting the gas desulfurizer. All other product analyses are of the last sample taken from the regenerator.

* Nominal size consist.

Run A1

Approximately 97% of the H_2S fed was removed in the gas desulfurizer. Gas exiting the bed contained about twice the calculated equilibrium H_2S concentration. However, only partial regeneration was achieved, and the CaS concentration continued to build up in the acceptor. Figure 33 presents the concentration of sulfur in solids exiting the gas desulfurizer and the regenerator as a function of time. Figure 34 gives the H_2S concentration in the dry gas exiting each vessel.

The hourly attrition rate was 2.5% of acceptor being fed, far higher than the same acceptor had given in the CO_2 cycle for the CO_2 Acceptor Process.(3) The run was shut down due to difficulties in switching the solids filters.

Run A2

Run A2 was a refined repetition of A1. The fluidizing velocity in the regenerator was lowered, and the wall temperature of the sulfur reactor was closely controlled. In Run A1 the wall temperature exceeded 1750°F and calcination of $CaCO_3$ may have occurred. For all later runs, the wall temperature did not exceed the bed temperature by more than 60°F.

As in A1, about 97% removal of H_2S was obtained in the sulfur reactor; this corresponds to twice the equilibrium H_2S content in the exit gas. Regeneration was incomplete, and the sulfur content of the acceptor went up with time. This is shown graphically in Figure 33.

The attrition rate was disastrously high, i.e., 18% of the acceptor fed per pass. Loss of inventory due to attrition forced an early shutdown.

The acceptor was soft when it came out of the regenerator. Yet all of the attrited material was collected in the sulfur reactor filters. This led to the conclusion that attrition occurred in the feeder, the pick-up chamber, and the lift line to the gas desulfurizer. The feeder was disconnected from the lift line, and then, at atmospheric pressure, regenerator bed material from Run A2 was run through the feeder. About 2% attrition, as measured by the -150 mesh fraction, occurred in the feeder alone. Details are given below:

Feed: Run A2 Regenerator Bed Material

	Into Feeder, Wt. %	Out of Feeder, Wt. %
+28	0.1	2.0
28 x 35	70.5	67.0
35 x 48	17.6	17.9
48 x 100	6.9	7.0
100 x 150	1.3	1.5
150 x 200	0.7	2.5
-200	2.9	3.2

Run A3

Run A3 was to be made with 20 x 28 mesh acceptor which required a higher fluidizing velocity, 0.96 ft/sec. It was not possible to establish an even temperature profile in the sulfur reactor with such a high gas rate, and H_2S feeding was never initiated. As in previous runs, the attrition rate was high.

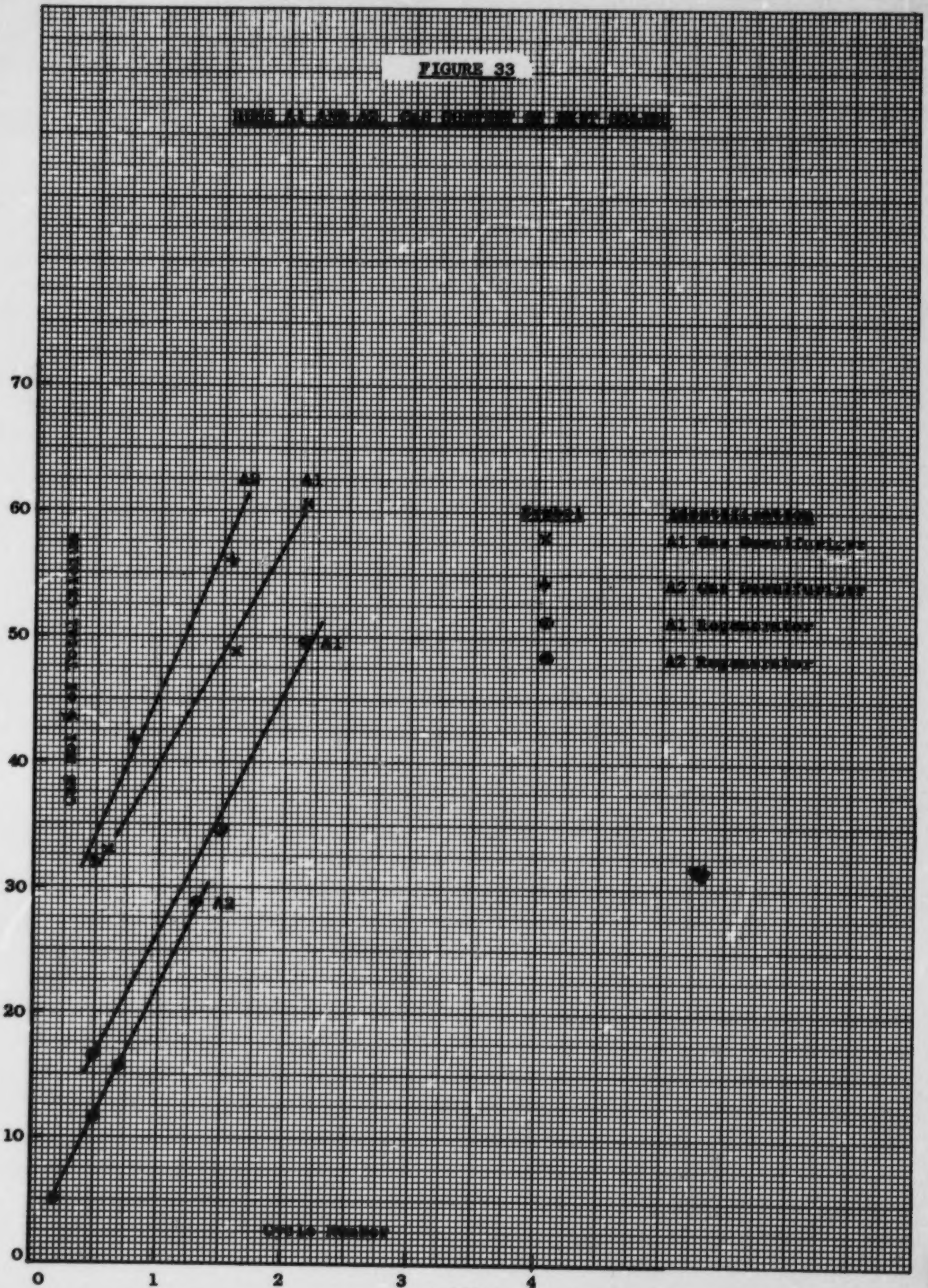


FIGURE 33

RUNS A1 AND A2. [illegible]

K+E 10 X 10 TO ½ INCH 46 1323
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

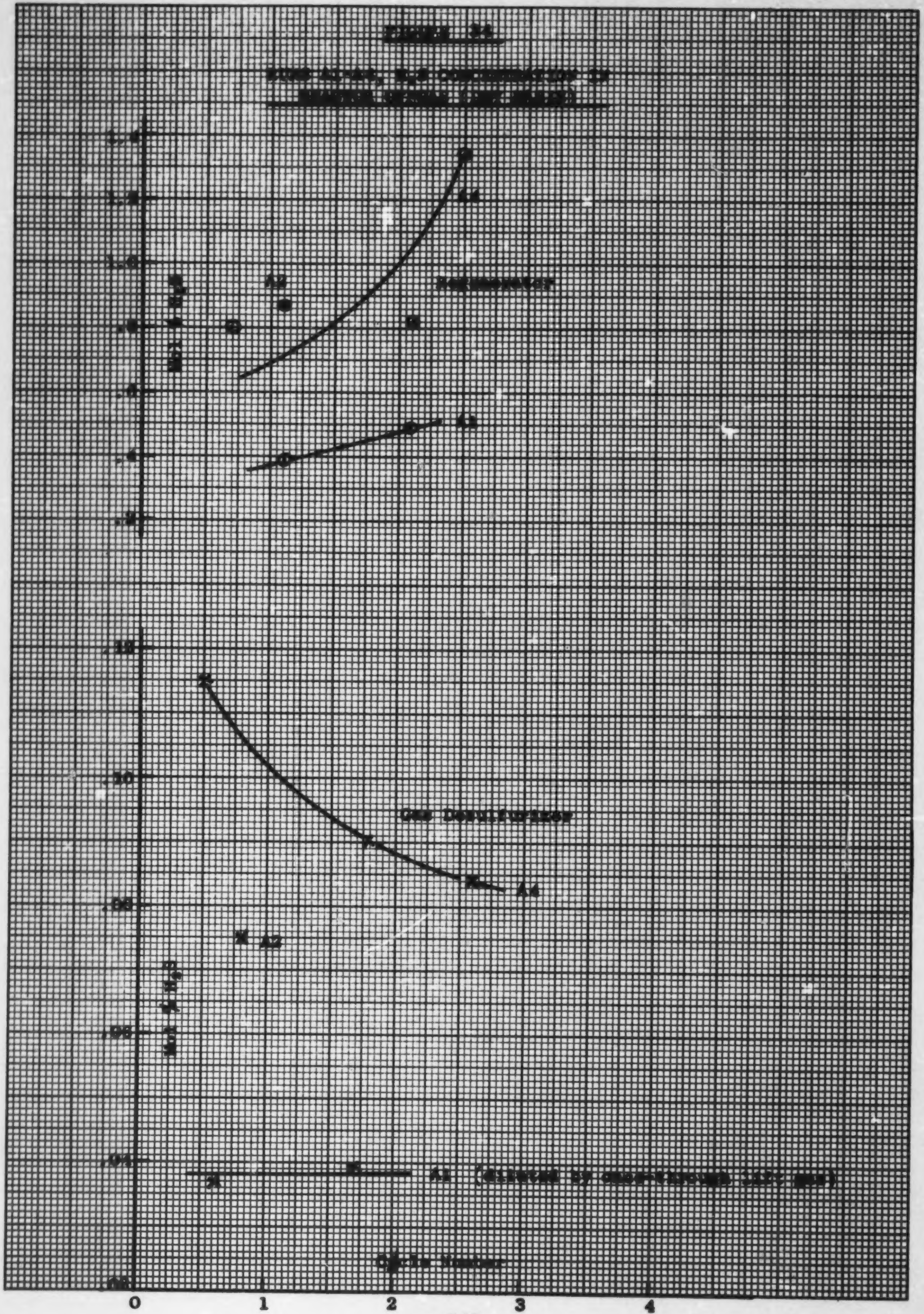


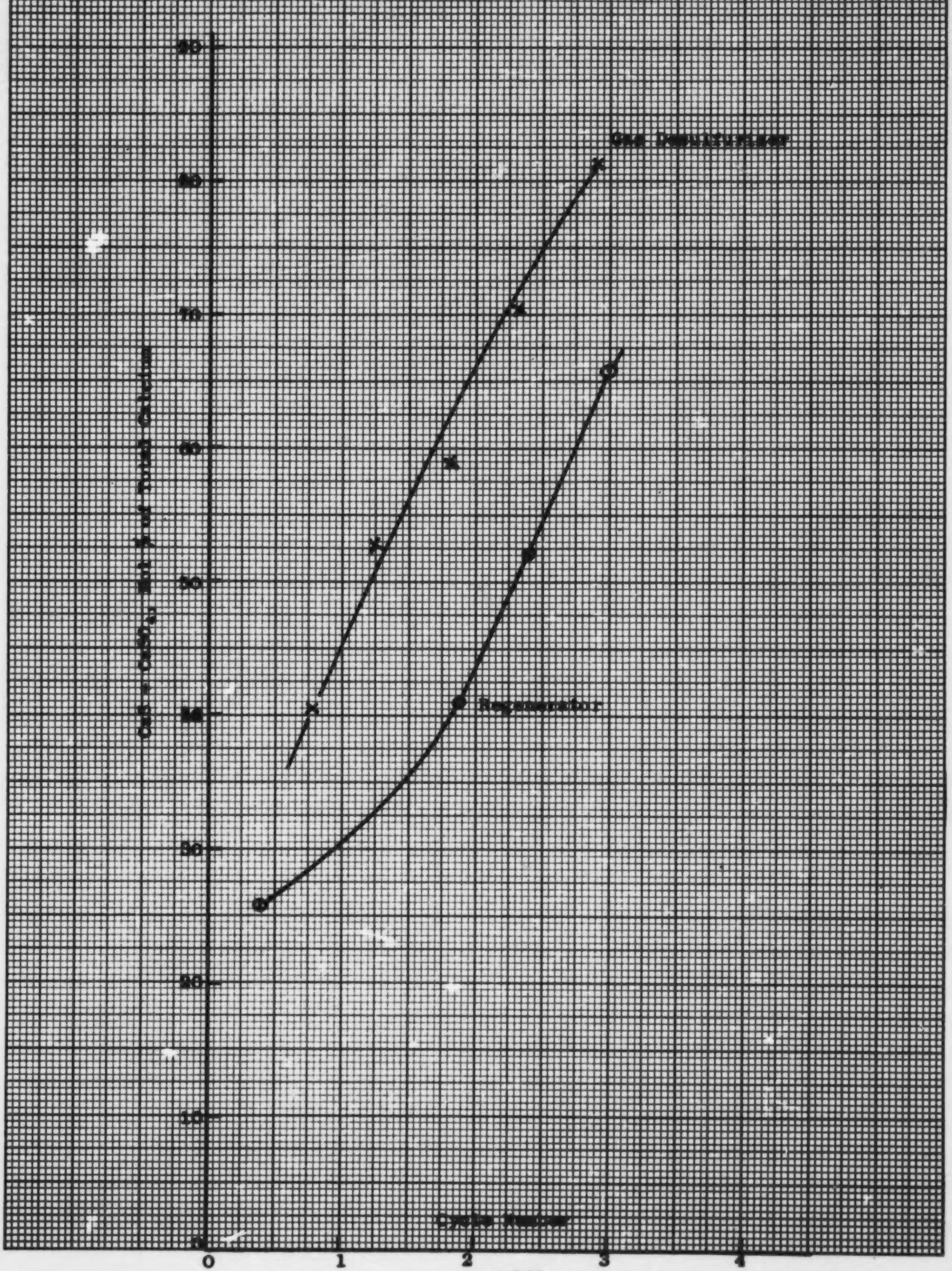
FIGURE 34

[illegible]

K+E 10 X 10 TO ½ INCH 46 1323
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

FIGURE 25

RUN A-4 MOLAR SULFUR CONTENT OF [illegible] SOLIDS



K+E 10 X 10 TO ½ INCH 46 1323
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

Run A4

On the premise that during the OCR CO_2 Acceptor development work dolomite had been hardened due to the formation of transient liquid from $CaSO_4$-CaS, air was added to the regenerator to convert about 4% of the calcium to $CaSO_4$. There was no build-up of sulfate with cycling, since it was reduced in the gas desulfurizer. The attrition rate was lower than in the comparable Run A2 but was still unacceptably high. Either 1600°F is too low a temperature for transient liquid formation or the sulfate was reduced before liquid formation could occur.

An interesting result of the run was that about 10% of the total sulfur in the regenerator offgas was elemental sulfur. Previously, only trace quantities had been collected.

The sulfur contents of product gases and solids are given in Figures 34 and 35, respectively. Again, H_2S removal was good in the gas desulfurizer and regeneration was incomplete. The concentration of H_2S in the regenerator offgas went up as the sulfur content of the acceptor increased. The run was terminated because of attrition of the acceptor inventory.

The attrition from Run A1 was lower than that from Runs A2, A3, and A4. Conditions in Run A1 were substantially different from the others only in that the wall temperature in the sulfur reactor was higher in Run A1. Hardening may have involved calcination or sintering because of the wall temperature exceeding 1750°F.

The initial level of CaO conversion to CaS for Runs A1, A2, and A4 was high. For Run A4 this was expected since the gas desulfurizer bed was presulfided before circulation of solids began. In Runs A1 and A2, it is believed that extra H_2S was fed while the rotameter was being adjusted. This adjustment is difficult and large slugs of liquid H_2S can get through while it is being made.

Run A18

Run A18 was made at conditions duplicating Run A4, except that air was not added. The attrition rate of Tymochtee dolomite in Run A4 was lower than in the roughly comparable Run A2, but still too high at 5.6%. Run A2 was made with 28 x 35 Tyler mesh stone and a lift gas rate of 158 SCFH; Run A4 was made with 35 x 48 mesh stone and a lift gas rate of 92 SCFH. While the results of Run A4 were encouraging with respect to hardening, the lesser lift gas flow may also have reduced attrition, thereby confounding the experiment.

Run A18 was made with 35 x 48 mesh Tymochtee stone and a low lift gas rate to more closely duplicate Run A4. No air was used. The attrition rate was 4.9% compared to 5.6% in Run A4. It is concluded that hardening due to transient liquid formation did not occur in Run A4. The results imply that attrition occurs mostly in the solids pick-up chamber and lift line, the flow rate of lift gas and the particle size being an important factor.

Although hardening due to transient liquid formation did not occur in Run A4, such hardening would be expected if the two-stage process pictured in Figure D-1 of Appendix D were used. The two-stage modified sulfur recovery system is described in detail in Appendix D. CaS is oxidized to $CaSO_4$ in a riser reactor, and the temperatures should be high enough to induce transient liquid formation with the attendant hardening of the stone. The $CaSO_4$ then acts as an oxidizing agent toward Squires reactor product gas to produce a Claus feed.

Having established the objective of checking the attrition rate, the steam/CO_2 ratio in the regenerator was also altered from 1/1 to 0.5/1 and then to 1.7/1. The goal was to find quickly whether this was a key kinetics variable. Results are detailed in Table 38 and Figure 36, and are summarized below:

Run Number	A18-1	A18-2	A18-3
Mol % CaS in Feed to Regenerator	35.7	52.5	70.5
Mol % of Entering CaS Converted to $CaCO_3$	18	21	17
H_2O/CO_2	1.00	0.53	1.72
Cycle Number	2.0	3.3	5.6

There is no marked effect of variation of the steam/CO_2 ratio. However, the results are obscured by the inevitable increase in acceptor CaS content with increasing number of cycles.

The experiment should be repeated, using three separate runs.

C. Dolomite from CO_2 Acceptor Process

In Run A6, the feed was a composite of acceptors which had been used in bench-scale development of the CO_2 Acceptor Process under the Office of Coal Research (OCR). About 40% of the calcium was in the form of inactive CaO. This material had shown a low rate of attrition in the previous program, and when cycled in the presence of H_2S, the attrition rate remained low, about 0.2%.

Run conditions are detailed in Tables 42 and 43. Based on the original Ca present in the stone, 42% of the Ca was in the form of inactive CaO. Conversion was set for 10% Ca conversion of the remaining 58% of the Ca. The initial absorption of H_2S was good and then rapidly declined after seven cycles. The regeneration step was incomplete, but instead of improving, as the CaS content of the acceptor increased, exit H_2S content remained the same. This is presented in Tables 39 and 40, and graphically depicted in Figures 37 and 38.

At the end of the run, the solids feed was stopped and both vessels were run as batch beds for 150 minutes. This was done to see whether further regeneration would occur. The H_2S content of regenerator offgas fell from 0.37% to 0.06%, i.e., conversion dropped to a negligible level. Based on analysis of regenerator solids, the CaS content fell from 30% to 28%. There also was an increase in the CaS content in the gas desulfurizer from 42% to 50%.

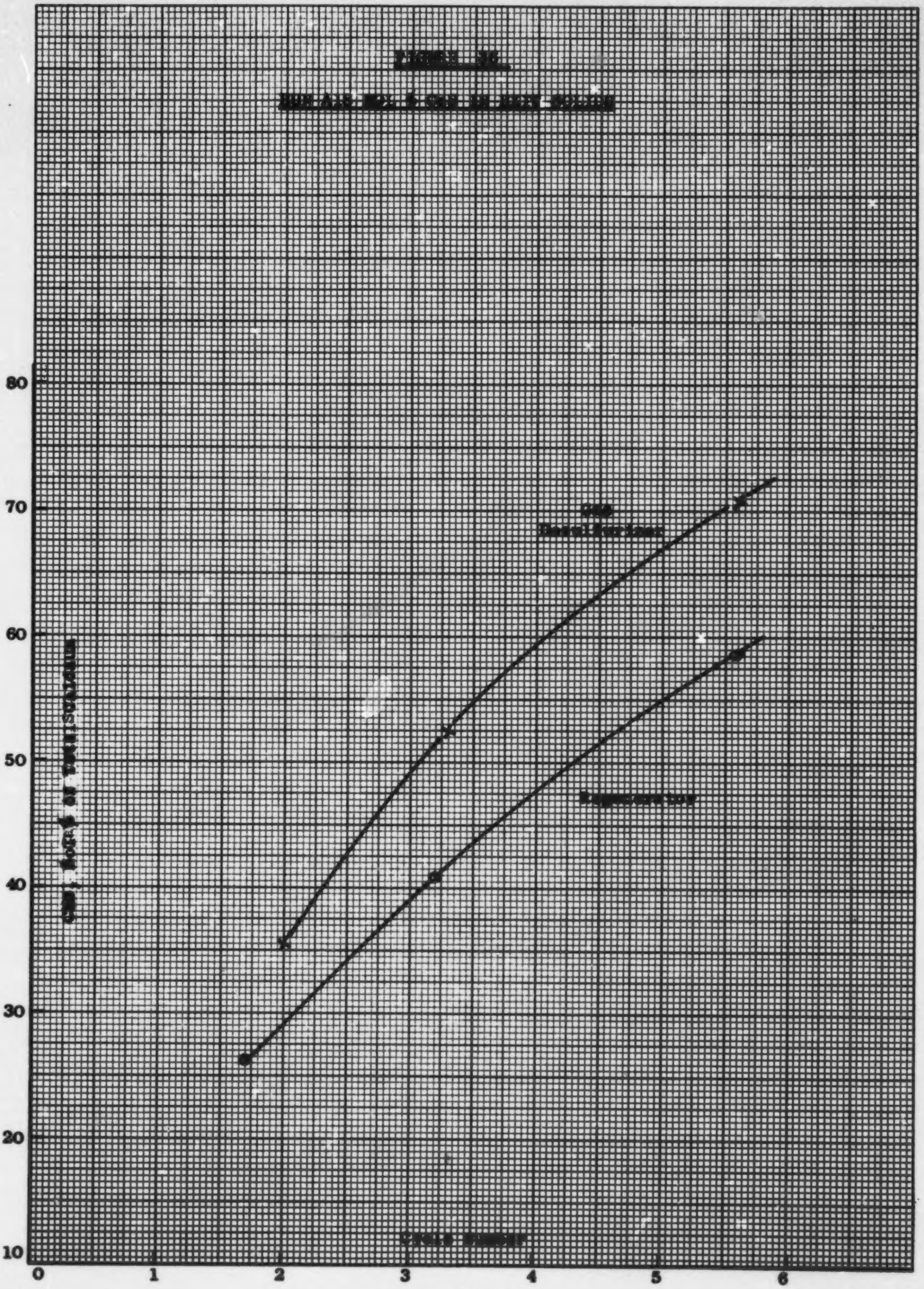
Run A6 showed that there is nothing about our run conditions which causes weakening of the stone upon cycling. By implication, a strong fresh dolomite should perform well with respect to both attrition and H_2S removal.

About 50% of the $CaCO_3$ was unreactive toward H_2S. Similarly, only a portion of the CaS which was formed was easily regenerated in the "Squires" reactor. Since this stone had an unusual history, there is no way to predict whether such a problem might become important to a freshly cycled dolomite.

D. Runs with Canaan Dolomite Feed

Run A7

Run A7 was made at simulated process conditions to test the activity and attrition resistance of Canaan dolomite from Connecticut. The attrition rate was low, about



K+E 10 X 10 TO ½ INCH 46 1323
7 X 10 INCHES MADE IN U.S.A.
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Table 42

Conditions and Results for Gas Desulfurizer With Dolomite Feed From CO_2 Acceptor Process

System Pressure: 15 atm. (206 psig)
System Temperature: 1600°F

Run Number	A6
Acceptor Size Consist, Tyler Mesh	20 x 35
Feed Rate, lb/hr (half calcined basis)	11.3
Solids Residence Time, min.	24
Input, SCFH	
Recycle to Bed	350
H_2S	1.7
CO_2	66
H_2	74
H_2O	29
N_2	87
Purges (CO_2) to Bed	5
Purges (N_2) above Bed	15
Recycle Acceptor Lift Gas, above Bed	90
Output in Cycle:	1-2
Exit Gas Rate, SCFH (dry basis)	211
Composition, Mol %	
H_2	6.2
CO	20.2
CO_2	13.7
N_2	59.8
H_2S	.105
Outlet Gas, Top of Bed	
Composition, Mol %	
H_2O	12.2
H_2	5.6
CO	18.2
CO_2	12.4
N_2	51.5
H_2S	.0947
Flow Rate, SCFH, Top of Bed	622
Fluidizing Velocity, ft/sec	.90
Attrition, % of Feed Rate	.15
Duration of Circulation with H_2S Feed, hr	24.9
Removal of Feed Sulfur, %	87
Removal of Feed plus Recycle Sulfur, %	72
% H_2S in Outlet/Equilibrium % H_2S	2.1
Conversion of Acceptor/Pass, mol %	8

TABLE 43

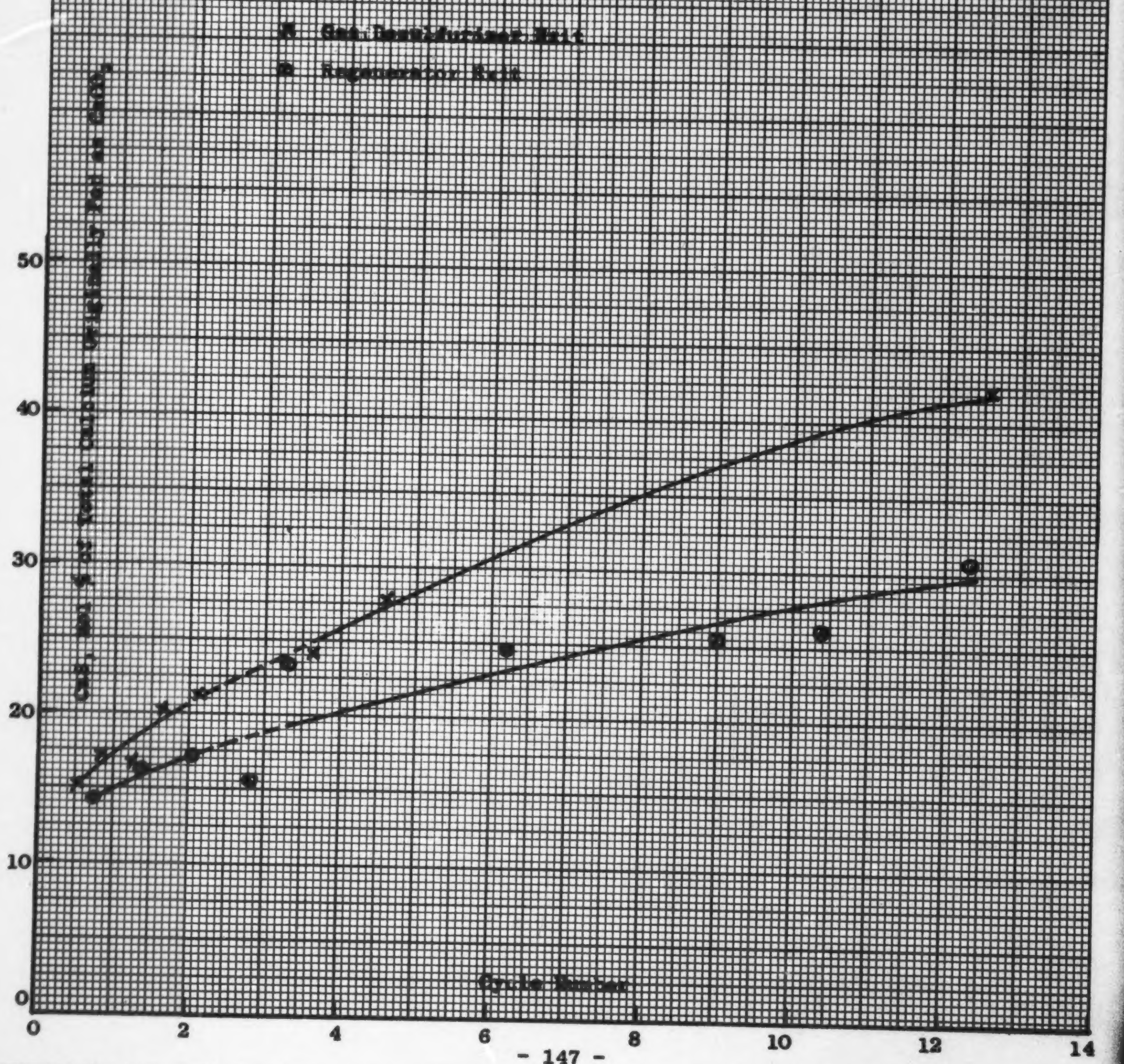
Conditions and Results for Regenerator with Dolomite from CO_2 Acceptor Process

System Pressure: 15 atm. (206 psig)
System Temperature: 1300°F

Run Number	A6
Solids Residence Time, minutes	27
Input, SCFH	
H_2O	131
CO_2	162
Purges (N_2) to Bed	10
Purges (N_2) above Bed	10
Purges (CO_2) above Bed	5
Output in Cycle:	1-2
Exit Gas Rate, SCFH (dry basis)	185
Composition, Mol %	
CO_2	89
N_2	11
H_2S	.26
Outlet Gas, Top of Bed	
Composition, Mol %	
H_2O	43.5
CO_2	53.1
N_2	3.2
H_2S	.16
Flow Rate, SCFH, Top of Bed	301
Fluidizing Velocity, ft/sec	.85
Regeneration of Acceptor, Mol %	2.6

FIGURE 37

RUN 46 - CaS CONTENT OF ACCEPTOR



K+E 10 X 10 TO ½ INCH 46 1323
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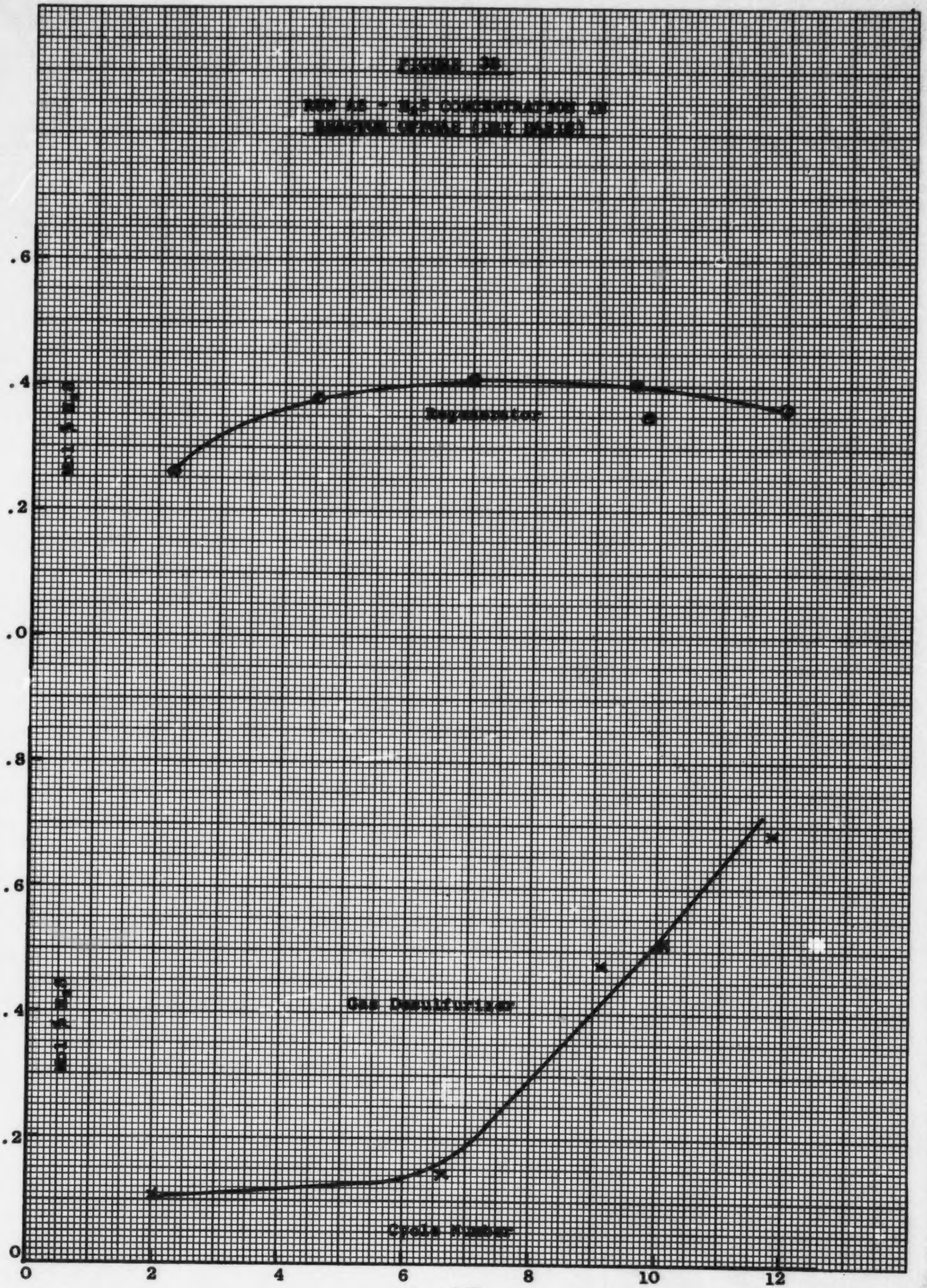

FIGURE 38

RUN 45 - H_2S CONCENTRATION IN

[illegible] (DRY BASIS)

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0.8%, for the entire run. Good H_2S removal in the gas desulfurizer was maintained for about eleven cycles. Breakthrough occurred in the gas desulfurizer because of the build up of CaS which resulted in insufficient $CaCO_3$ to react with the input of H_2S.

Details of the run conditions are given in Tables 44 and 45. The sulfur-bearing contents of exit gases and solids are given in Tables 39 and 40, respectively. The data are presented graphically in Figures 39 and 40.

When H_2S breakthrough occurred in the gas desulfurizer, the solids feed was stopped and both vessels were run as batch beds for two additional hours. This was done to see whether additional regeneration would occur or not. There was a possibility that the CaS was "dead" and might not react any further. After two hours, the $CaCO_3$ content of acceptor in the regenerator rose from 15 to 24 mol %, thereby showing that additional regeneration would occur if residence time were increased in the regenerator.

Several encouraging conclusions may be drawn from Run A7:

1. The $CaCO_3$ in dolomite is effective in removing H_2S up to high conversions in the solid. At the end of Run A7, 98% of the $CaCO_3$ in the solid had been converted to CaS.

2. The attrition problem encountered with the Tymochtee stone is not common to all dolomites. The average attrition rate for Run A7 was 0.8% of the acceptor feed rate.

3. The regeneration reaction works to the extent that at least moderate regeneration of $CaCO_3$ from CaS occurred with a forty minute residence time.

At the end of Run A7, about 70% of the inlet H_2S to the desulfurizer was being recovered in the regenerator with a solids residence time of forty minutes. This corresponded to conversion of about 13 mol % of the calcium in the stone. If conversion were to stay constant in the regenerator and the H_2S input were reduced, it might be possible to circulate acceptor for a large number of cycles at 13% conversion per pass between ca. 93 and 80% CaS in the solid while maintaining close to equilibrium H_2S removal in the sulfur reactor.

During Run A7, small amounts of sulfur in the regenerator condensate caused drainage problems. In later runs, about 5% of hydrogen was added to the regenerator feed to inhibit dissociation of H_2S.

Runs A15 and A16

Two runs were made with Canaan dolomite at 1100°F in the regenerator instead of 1300°F as used in Run A7. The run conditions are given in Tables 44 and 45, and results are plotted in Figures 41 through 44.

Run A15 was carried out at the same conditions as Run A7, except for the lower regenerator temperature. In A15 breakthrough occurred in the gas desulfurizer at about 6 cycles as compared with after about 10 cycles in A7. Gas analyses had not been taken prior to this, but analyses of the solids indicate that good pickup was being achieved.

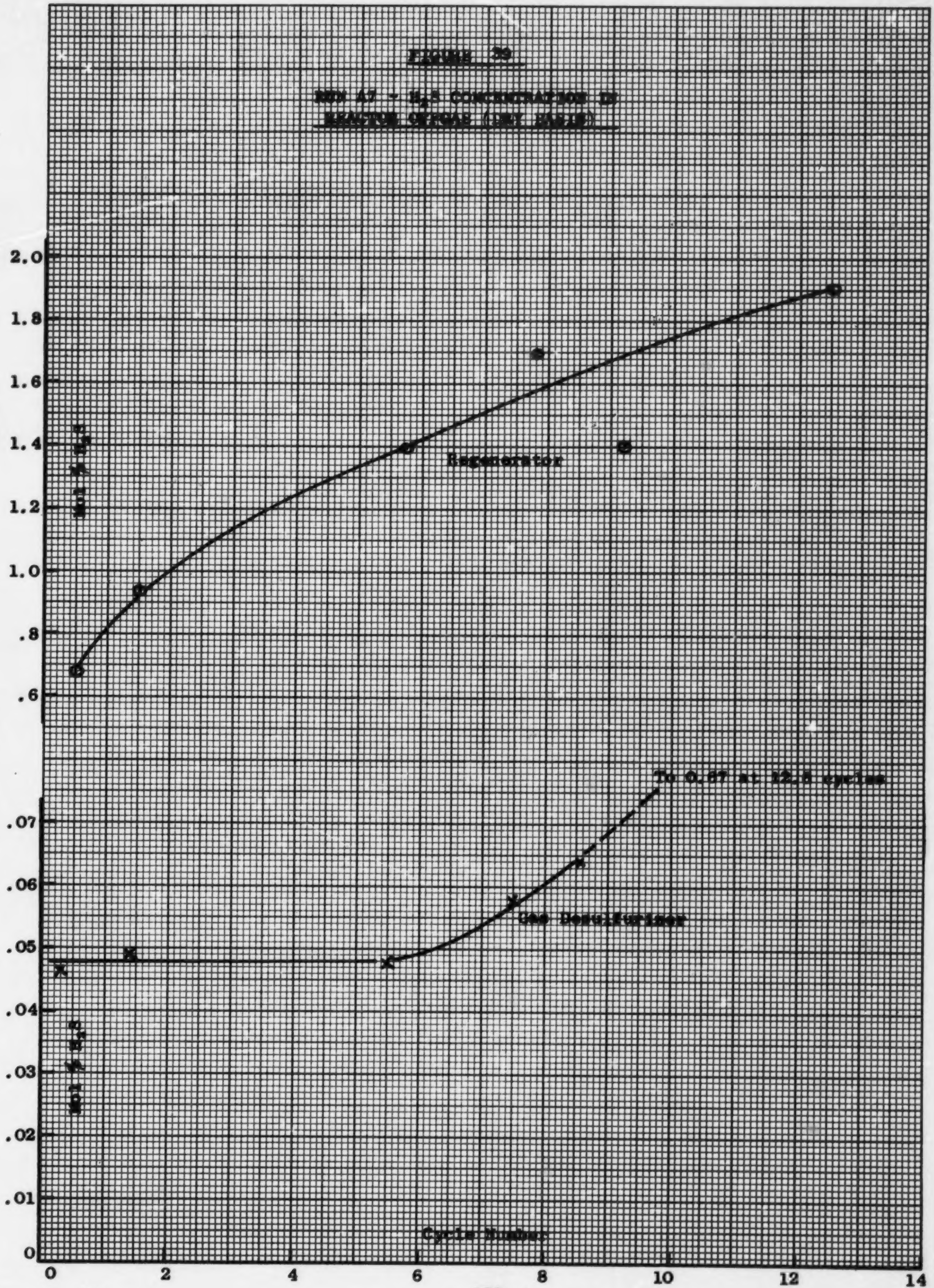

FIGURE 39

RUN 47 - H_2S CONCENTRATION IN REACTOR OFFGAS (DRY BASIS)

K•E 10 X 10 TO ½ INCH 46 1323
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FIGURE 40

RUN A7 CaS CONTENT OF ACCEPTOR

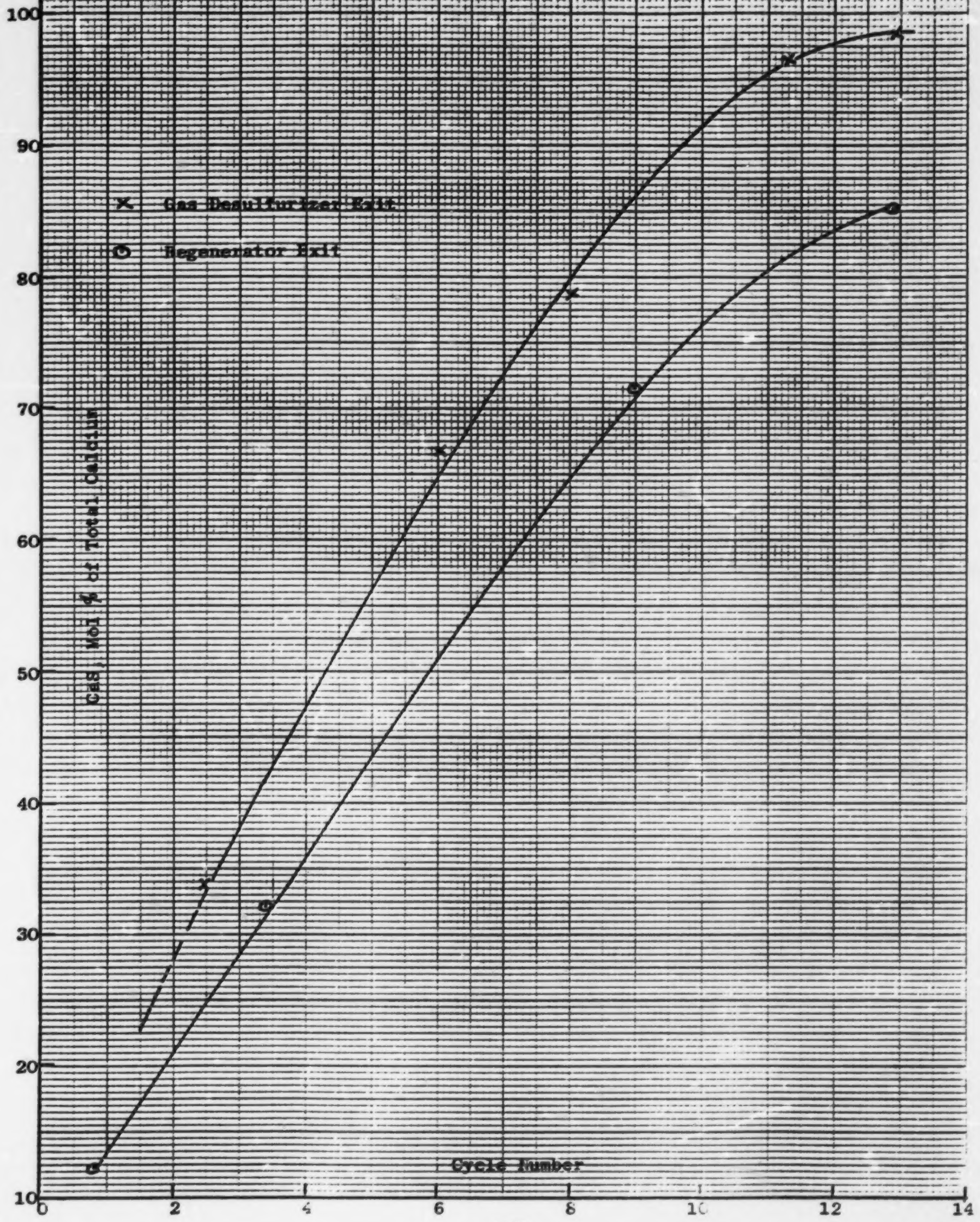


Table 44

Conditions and Results for Gas Desulfurizer with Canaan Dolomite Feed

System Pressure: 15 atm (206 psig)
System Temperature: 1600°F

Run Number	A7		A15	A16
Acceptor Size Consist, Tyler Mesh	28 x 35		28 x 35	28 x 35
Feed Rate, lb/hr (half-calcined basis)	6.5		6.7	3.3
Solids Residence Time, minutes	32		32	65
Input, SCFH				
Recycle to Bed	175		178	178
H_2S	3.5		3.5	1.8
CO_2	54		54	54
H_2	73		73	73
H_2O	-		-	-
N_2	96		96	96
Purges (CO_2) to Bed	5		5	5
Purges (N_2) above Bed	15		15	15
Recycle, Acceptor Lift Gas, above Bed	71		71	71
Output, SCFH in Cycle	1-2		6-7	1-3
Exit Gas Rate, SCFH (dry basis)	215		213	215
Composition, Mol %				
H_2	17		17.5	18.2
CO	18		17.9	18.0
CO_2	12	(1)	9.93	9.74
N_2	53		54.4	54.0
H_2S	.05		.207	.048
Outlet Gas, Top of Bed				
Composition, Mol %				
H_2O	9.8		10.0	9.47
H_2	16		16.4	17.1
CO	17		16.8	16.9
CO_2	11		9.28	9.18
N_2	46		47.3	47.3
H_2S	.046		.194	.045
Flow Rate, SCFH, Top of Bed	416		418	418
Fluidizing Velocity, ft/sec	.60		.60	.60
Attrition, % of Feed Rate	0.7		.77	.89
Duration of Circulation with H_2S Feed, hrs	25.5		35.1	42.7
Removal of Feed Sulfur, %	97		87	94
Removal of Feed + Recycle Sulfur, %	95		79	90
% H_2S in Outlet/Equilibrium % H_2S	1.4		6.8	1.7
Conversion of Acceptor/Pass, mol %	19		16	18

(1) Estimate.

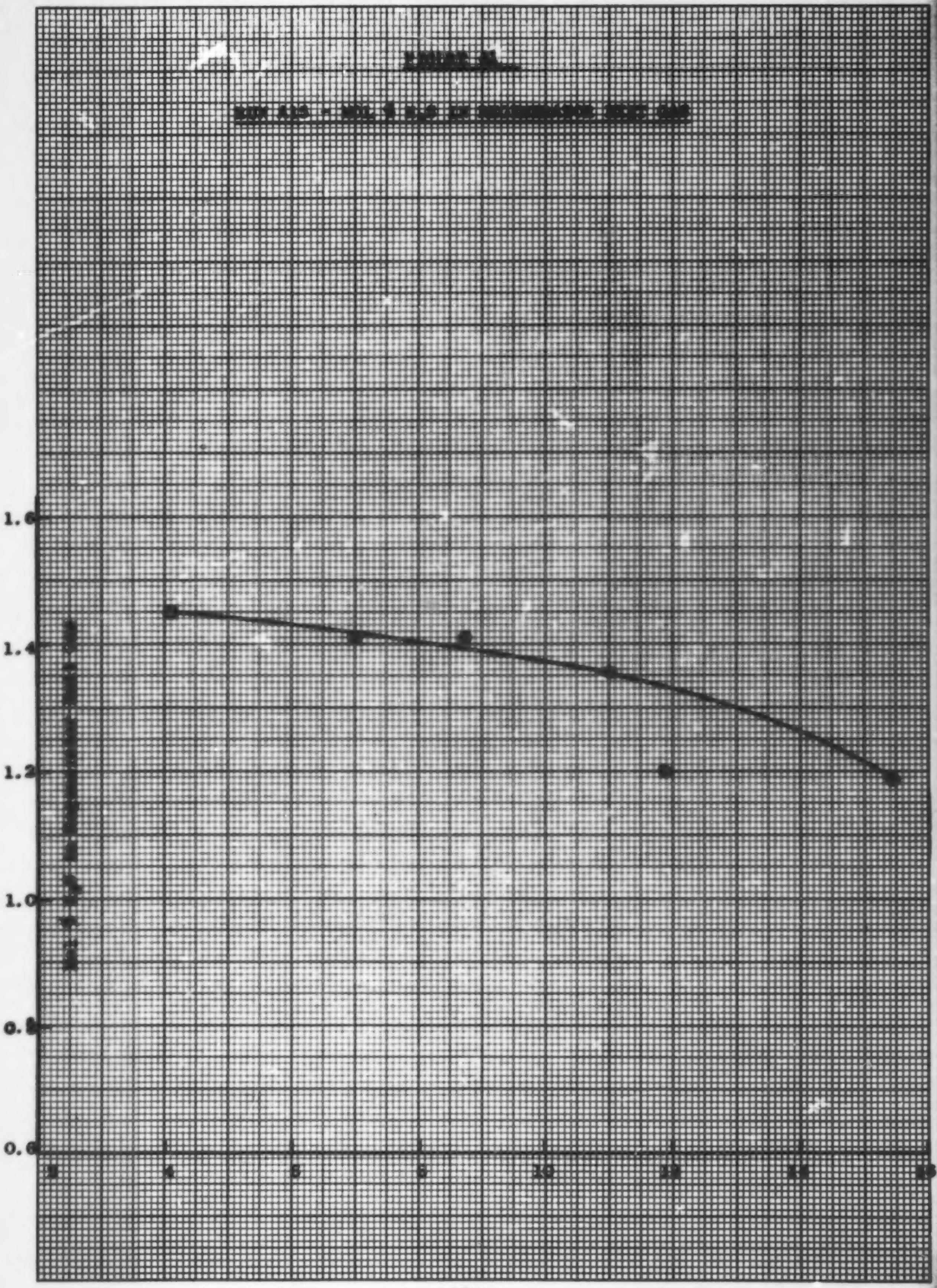
Table 45

Conditions and Results for Regenerator with Canaan Dolomite Feed

System Pressure: 15 atm. (206 psig)

Run Number	A7	A15	A16
Solids Residence Time, minutes	37	36	74
Temperature, °F	1300	1100	1100
Input, SCFH			
H_2O	110	100	109
CO_2	110	118	118
H_2	0	12	12
Purges (N_2) to Bed	8	8	8
Purges (N_2) above Bed	10	10	10
Purges (CO_2) above Bed	5	5	5
Output in Cycle	1-2	6-7	1-3
Exit Gas Rate, SCFH (dry basis)	133	154	152
Composition, Mol %			
CO_2	85.7	78.4	77.4
N_2	13.5	11.4	12.8
H_2S	0.7	1.41	.456
H_2	ND	8.0	8.3
CO	ND	.76	1.01
COS	ND	.02	Trace
Outlet Gas, Top of Bed			
Composition, Mol %			
H_2O	48.3	41.6	44.1
CO_2	47.8	48.5	46.0
N_2	3.5	3.2	3.9
H_2S	0.4	.91	.282
H_2	--	5.15	5.14
CO	--	.49	.63
COS	--	.01	Trace
Flow Rate, SCFH, Top of Bed	228	238	245
Fluidizing Velocity, ft/sec	.63	.60	.61
Regeneration of Acceptor, Mol %	5.1	11.5	7.5

ND - Not Determined.



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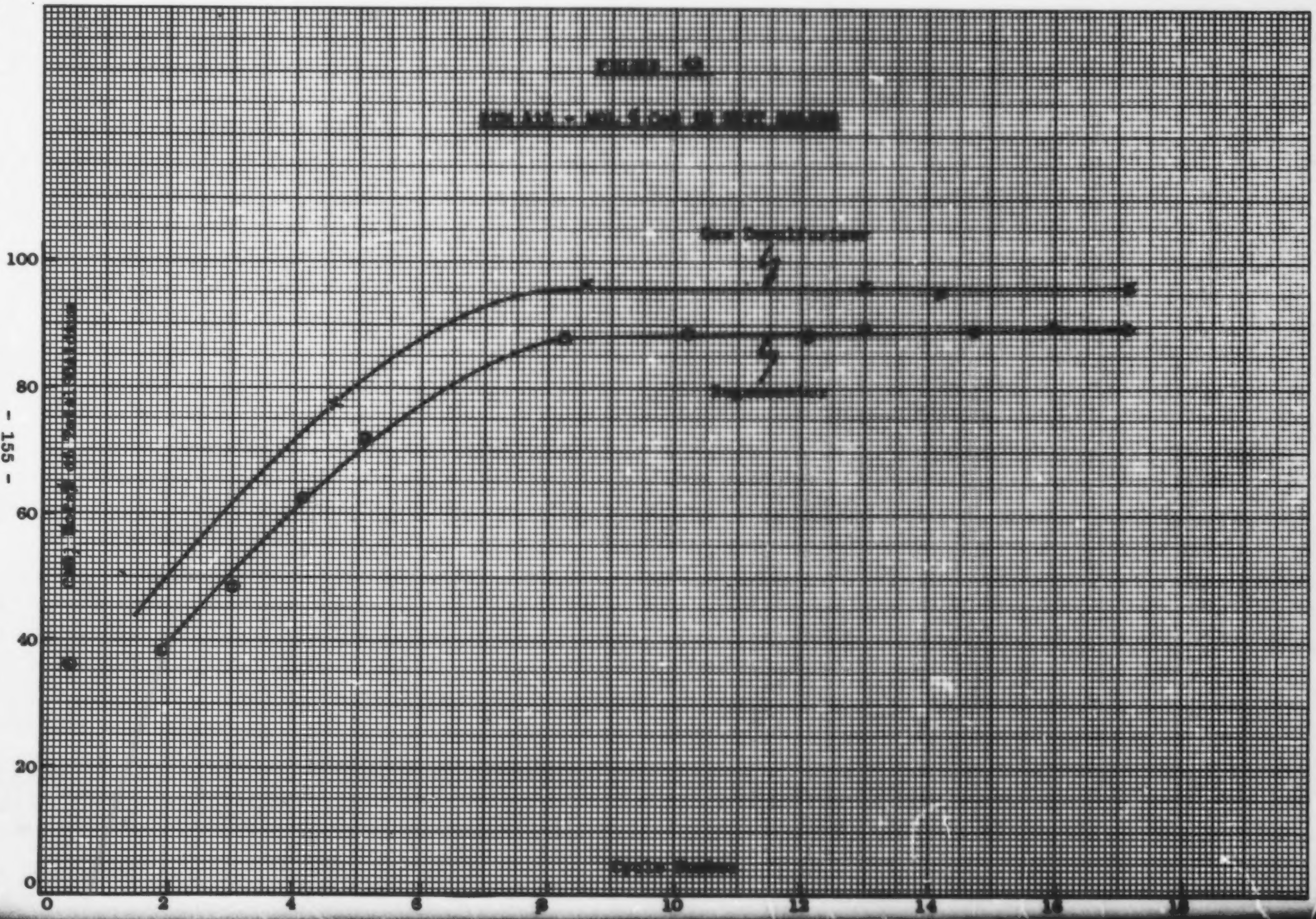

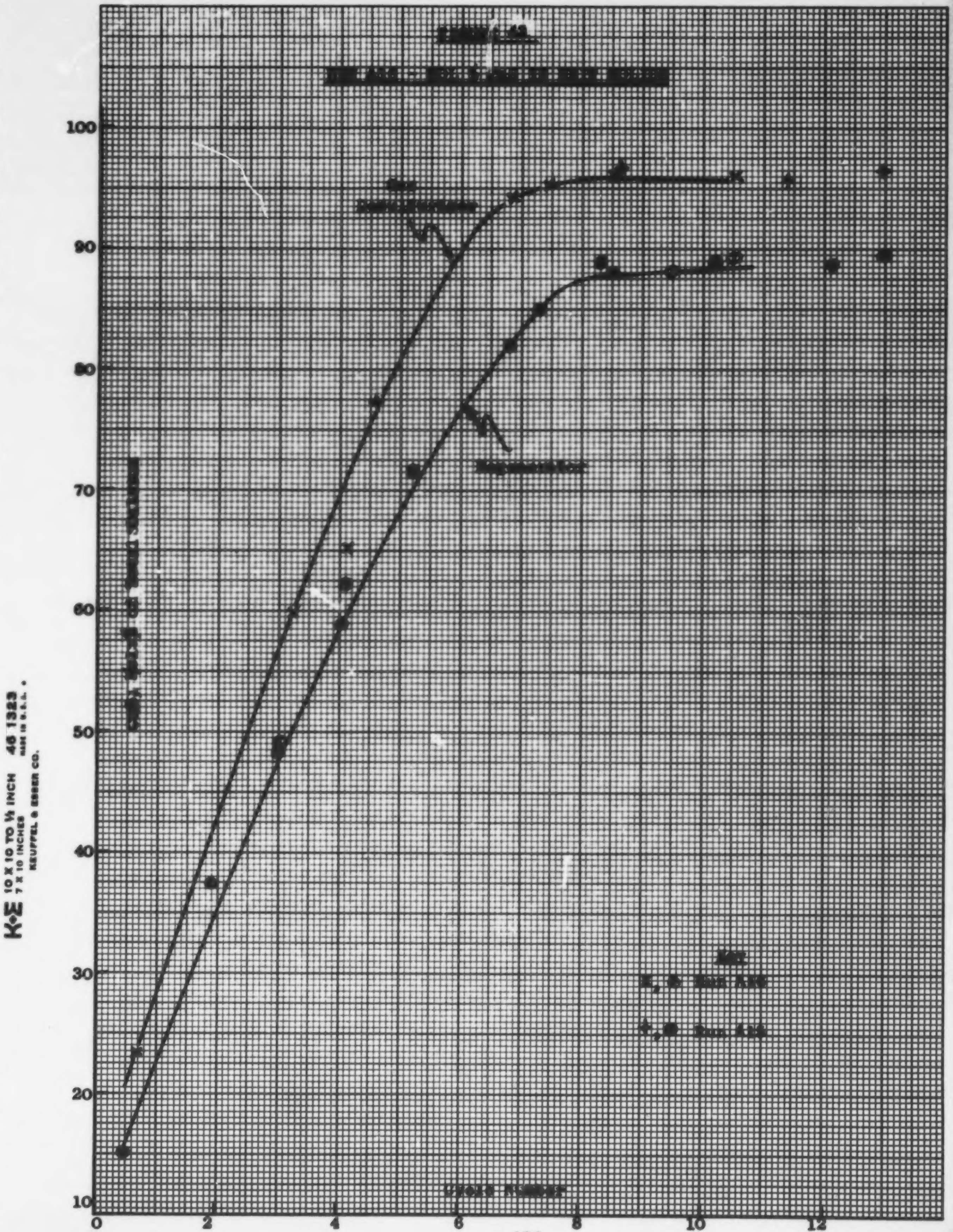
100
90
80
70
60
50
40
30
20
10
0
2
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12
K+E 10 X 10 TO ½ INCH 46 1323
7 X 10 INCHES MADE IN U.S.A.
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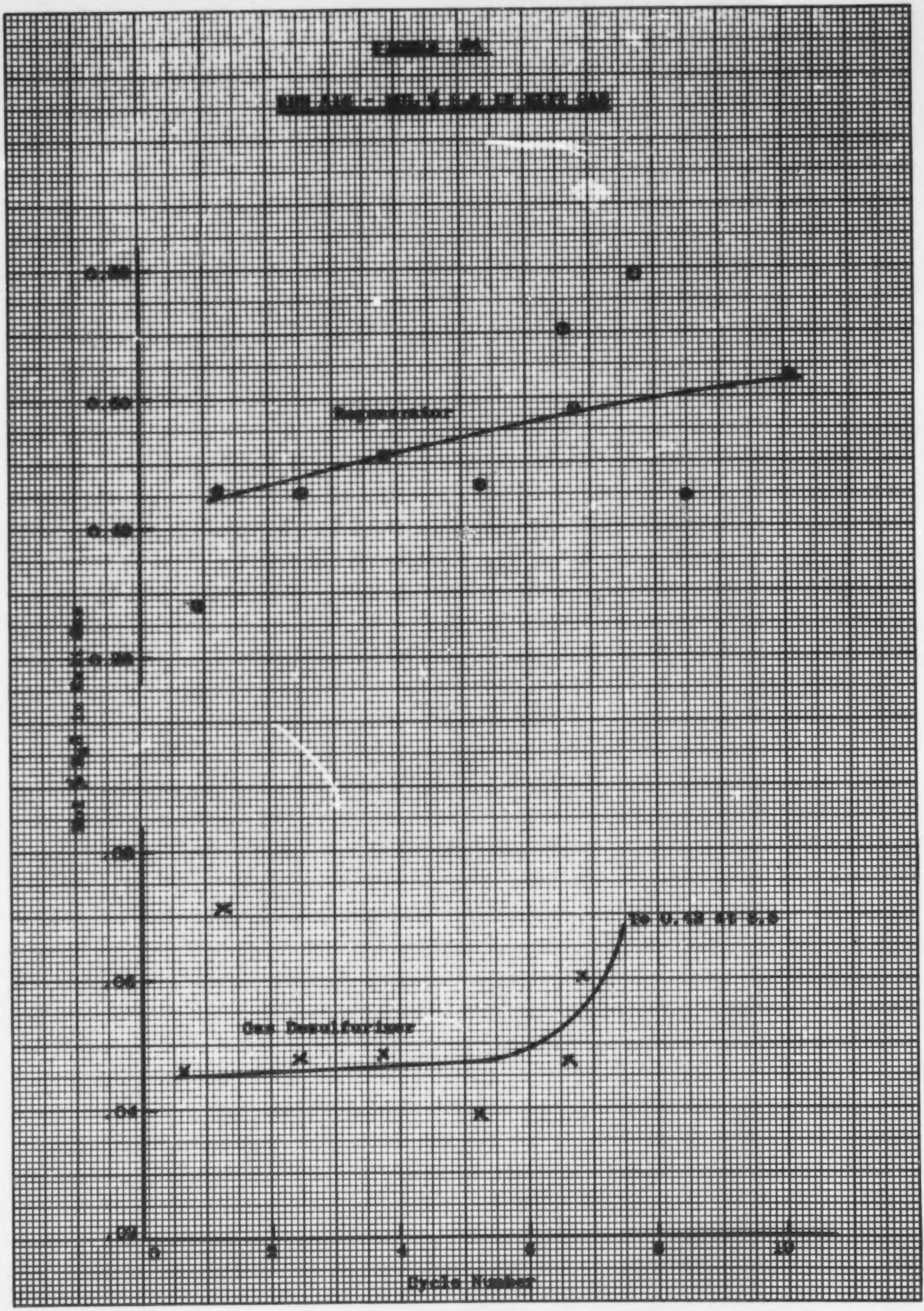

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The progress of the run was defined by the CaS content of solids, which is given in Figure 42. Where the desulfurizer curve reaches its plateau, the reduction in CaS content in going through the regenerator is 8 mol % absolute. For Run A7, it was 13%. Going from 8% to 13% conversion for a 200°F change in temperature is equivalent to an activation energy of the order of 7-11 Kcal/gm mol depending on the mechanism assumed. The system is thus relatively insensitive to change in temperature as long as equilibrium is not limiting.

A very important result of Run A15 is that the observed decline in activity was quite low as cycling was continued. From cycle 8 to cycle 17, the amount regenerated dropped from 8 mol % to 6 mol %. This is confirmed by the gas data presented in Figure 41 which shows the exit H_2S concentration from the regenerator slowly dropping from 1.4% to 1.2%.

More data are required for confirmation, but it appears that good activity could be sustained for a large number of cycles under Run A15 conditions if the circulation rate were increased such that only 6-8% of Ca were sulfided per pass through the sulfur reactor.

The same tentative conclusion applies to Run A7 conditions, but here the amount of Ca sulfided per pass could be increased to 13%.

Run A16 was comparable to A15 with the feed rates of H_2S and acceptor halved. This maintained the same conversion of acceptor per cycle, and doubled the residence time of acceptor in both vessels. It was hoped that increased residence time in the regenerator would increase the degree of regeneration per pass.

Figure 43 presents the solids data from Run A16 together with data from Run A15. There was no effect of increasing the residence time. The data points from both runs fall on the same curves.

The exit gas H_2S content is given in Table 39 and in Figure 44. Since only half the usual H_2S was fed, the H_2S content of the regenerator offgas was correspondingly lower.

At the end of Run A16, acceptor circulation was halted and the vessels were run as batch beds. Samples were withdrawn from the regenerator and analyzed. At the end of Run A16, the initial bed feed solids contained 3.6 mol % $CaCO_3$ and the final bed product 11.7 mol % of $CaCO_3$ after a residence time of 75 minutes. An additional holding time of ten hours increased the $CaCO_3$ content to only 17.5%.

The conclusion to be drawn from the comparison of Run A15 with A16, and from the experiment at the end of A16 is that most of the CaS is in a form which is unreactive, and increasing the residence time will provide only a marginal improvement in conversion in the regenerator. It seems that the conversion of CaS per cycle is limited to about 6-8% per pass at 1100°F regardless of residence time.

Density of Sulfided Product

As dolomite is sulfided, its density tends to decrease as $CaCO_3$ is converted to CaS. Table 46 lists the density of several sulfided samples. Although density decreased with degree of sulfidation, the change was not as great as would have

Table 46

Density of Sulfided Canaan Dolomite

Run No.	Cycle Number	Mol % CaS	Density(1) Lb/ft^3
A7	.8	9.6	142.6
	5.7	48.0	139.0
	12.3	85.0	131.6
A15	0	0	176.0(2)
	.4	35.8	134.9
	8.3	88.6	130.5
	12.1	88.6	130.8
	17.1	89.9	130.4
A16	10.5	88.3	126.3

(1) Measured in mercury at 1 atmosphere.

(2) Raw uncalcined feed.

been predicted from molecular weight calculations. The reasons for this are not clear at this time. In Run A15, there was no change in density once the sample had been thoroughly sulfided.

E. Runs with Pennsylvania and Virginia Dolomites

Three runs were made to examine the attrition resistance of two other dolomites. Results are summarized in Tables 47 and 48.

The feed for Run A11 was supplied by G. & W. H. Corson, Inc., Plymouth Meeting, Pennsylvania. This stone gave an attrition rate of 9% of the feed rate. The run was shut down after three cycles due to depletion of the feed. Based on the analysis of solids and a single gas analysis, it was concluded that pick up of H_2S and subsequent regeneration were about the same as with other dolomites.

The James River Limestone Company supplied the Buchanan, Virginia dolomite which was the feed for Run A12. The run was shut down due to depletion of the feed as a result of a relatively high attrition rate of 4%.

The activity of the Buchanan dolomite was good and its performance on regeneration was at least equivalent to that of the Canaan dolomite as noted by the relatively high recovery of about 70% of the H_2S fed to the desulfurizer in regeneration of the acceptor (cf. Table 39).

Another possible criterion to judge the maintenance of activity is the divergence between curves representing the CaS content of acceptor leaving the sulfur reactor and regenerator, respectively, versus the number of cycles. As long as this divergence is maintained then regeneration is being achieved. The Buchanan dolomite also performed well based on this criterion as the curves in Figure 45 show.

The principal disadvantage of the Buchanan dolomite then is its relatively high attrition rate.

A sample of regenerator gas from Run A12 was found to contain COS, a component for which we did not usually check. Equilibrium considerations call for COS to be present at a level of about 3% of the H_2S.

For Run A19, the gas desulfurizer was run at 1650°F with Buchanan dolomite feed. The purpose was to see whether sufficient sintering would occur at the higher temperature to reduce the attrition rate. The run was similar to Run A12, except for the higher temperature and the need to increase the CO_2 content of the gas to prevent calcining at the hot walls. The attrition rate was 5.0%, compared to 4.1% in Run A12. It was concluded that hardening due to sintering does not occur in going from 1600 to 1650°F in the gas desulfurizer.

F. Runs with Limestone Feeds

Two varieties of limestone were tested to see whether the attrition problem experienced with dolomites would occur. Results are summarized in Tables 49 and 50 . Ruth, et al.(15) have found limestone and calcite to be inactive in the reaction of $CaCO_3$ with H_2S. On the other hand, Esso England(16) used 1691 limestone from Seneca Falls, New York in the reaction of CaO with H_2S and obtained good results.

Table 47

Conditions and Results for Gas Desulfurizer with Pennsylvania and Virginia Dolomite Feeds

System Pressure: 15 atm (206 psig)

Run Number	A11	A12	A19
Acceptor and Size Consist, Tyler Mesh	28 x 35 Plymouth Meeting, Pa. Dolomite	20 x 35 Buchanan, Va. Dolomite	28 x 35 Buchanan, Va. Dolomite
Temperature, °F	1600	1600	1650
Feed Rate, lb/hr (half-calcined basis)	7.0	7.4	7.2
Solids Residence Time, minutes	30	29	30
Input, SCFH			
Recycle to Bed	178	178	178
H_2S	3.5	3.5	3.6
CO_2	54	54	70
H_2	73	73	73
H_2O	-	-	-
N_2	96	96	96
Purges (CO_2) to Bed	5	5	5
Purges (N_2) above Bed	15	15	15
Recycle, Acceptor Lift Gas, above Bed	71	71	71
Output, SCFH in Cycle	1-2	2-3	4-5
Exit Gas Rate, SCFH (dry basis)	215	214	218
Composition, Mol %	(1)		(1)
H_2	18	20.7	13
CO	18	17.7	20
CO_2	10	9.2	16
N_2	54	52.4	51
H_2S	-	.11	.065
Outlet Gas, Top of Bed			
Composition, Mol %			
H_2O	10	9.8	6.6
H_2	17	19.4	13
CO	17	16.6	20
CO_2	9	8.66	15
N_2	47	45.6	46
H_2S	-	.106	.0635
Flow Rate, SCFH, Top of Bed	418	418	408
Fluidizing Velocity, ft/sec	.60	.60	.60
Attrition, % of Feed Rate	9.0	4.1	5.0
Duration of Circulation with H_2S Feed, hr	5.2	15.1	14.8
Removal of Feed Sulfur, %	Good	93	96
Removal of Feed + Recycle Sulfur, %	Good	88	93
% H_2S in Outlet/Equilibrium % H_2S	-	4.1	3.6
Conversion of Acceptor/Pass, mol %	ca. 20	16	18

(1) Estimated value. Gas chromatograph recorder not functioning.

Table 48

Conditions and Results for Regenerator with Pennsylvania and Virginia Dolomite Feeds

System Pressure: 15 atm. (206 psig)
System Temperature: 1300°F

Run Number	A11		A12	A19	
Solids Residence Time, minutes	34		33	34	
Input, SCFH					
H_2O	105		97	102	
CO_2	105		105	102	
H_2	11		11	11	
Purges (N_2) to Bed	8		8	8	
Purges (N_2) above Bed	10		10	10	
Purges (CO_2) above Bed	5		5	5	
Output in Cycle	1-2		2-3	4-5	
Exit Gas Rate, SCFH (dry basis)	135		133	130	
Composition, Mol %					
CO_2	77	(1)	72.5	76	(1)
N_2	13		16.5	14	
H_2S	1.41		1.68	1.32	
H_2	6		6.4	7.3	
CO	2	(1)	3.0	1.1	(1)
COS	ND		.03	ND	
Outlet Gas, Top of Bed					
Composition, Mol %					
H_2O	46		45.6	45.7	
CO_2	45		42.1	44	
N_2	3		5.5	4	
H_2S	.87		1.03	1.32	
H_2	4		3.9	4.5	
CO	1		1.8	.7	
COS	ND		.02	ND	
Flow Rate, SCFH, Top of Bed	220		217	210	
Fluidizing Velocity, ft/sec	.62		.61	.59	
Regeneration of Acceptor, mol %	10		11	9	

(1) Estimate. Gas chromatograph recorder not functioning.

ND - Not Determined.

FIGURE 45

RUN A12 - MOL % CaS IN EXIT SOLIDS

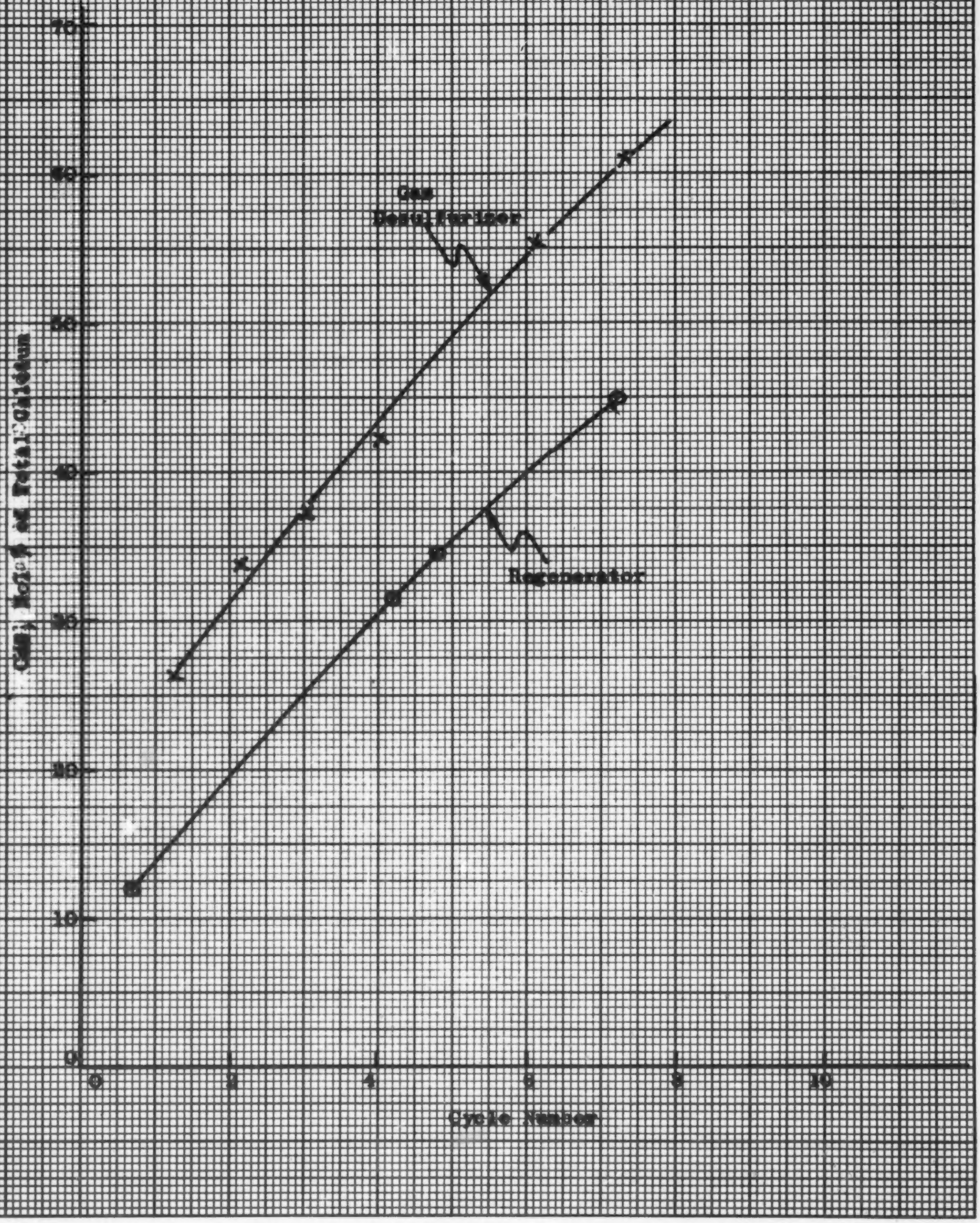

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Table 49

Conditions and Results for Gas Desulfurizer with Limestone Feeds

System Pressure: 15 atm (206 psig)
System Temperature: 1600°F

Run Number	A5		A13
Acceptor and Size Consist, Tyler Mesh	28 x 48 Nebraska Limestone		28 x 35 BCR-1691 Limestone
Feed Rate, lb/hr (half-calcined basis)	4.6		6.7
Solids Residence Time, minutes	60		34
Input, SCFH			
Recycle to Bed	165		200
H_2S	4.2		3.75
CO_2	48		59
H_2	63		90
H_2O	-		-
N_2	88		106
Purges (CO_2) to Bed	5		5
Purges (N_2) above Bed	15		15
Recycle, Acceptor Lift Gas, above Bed	85		71
Output, SCFH in Cycle	1-3		0-1
Exit Gas Rate, SCFH (dry basis)	191		223
Composition, Mol %			
H_2	16	(1)	15
CO	17		21
CO_2	11		9.7
N_2	55		54
H_2S	ca. 1.4		.11
Outlet Gas, Top of Bed			
Composition, Mol %			
H_2O	9	(1)	11
H_2	15		14
CO	16		19
CO_2	10		8.9
N_2	50		47
H_2S	> 1.3		.10
Flow Rate, SCFH, Top of Bed	373		480
Fluidizing Velocity, ft/sec	.54		.66
Attrition, % of Feed Rate	0.4		0.6
Duration of Circulation with H_2S Feed, hr	5.7		19.3
Removal of Feed Sulfur, %	< 8		94
Removal of Feed + Recycle Sulfur, %	< 8		83
% H_2S in Outlet/Equilibrium % H_2S	-		3.2
Conversion of Acceptor/Pass, mol %	< 1.1		19

(1) Estimated value.

Table 50

Conditions and Results for Regenerator with Limestone Feeds

System Pressure: 15 atm (206 psig)
System Temperature: 1300°F

Run Number	A5	A13
Solids Residence Time, minutes	68	39
Input, SCFH		
H_2O	126	109
CO_2	118	112
Air	7.7	-
H_2	-	12
Purges (N_2) to Bed	10	8
Purges (N_2) above Bed	10	10
Purges (CO_2) above Bed	5	5
Output, SCFH in Cycle	1-3	5-6
Exit Gas Rate, SCFH (dry basis)	146	146
Composition, Mol %		
CO_2	84.1	77
N_2	15.8	13
H_2S	0.06	1.44
H_2	-	6
CO	-	2
Outlet Gas, Top of Bed		
Composition, Mol %		
H_2O	52.7	46
CO_2	42.6	45
N_2	4.7	3
H_2S	.03	.88
H_2	-	4
CO	-	1
Flow Rate, SCFH, Top of Bed	277	238
Fluidizing Velocity, ft/sec	.78	.67
Regeneration of Acceptor, mol %	0.5	11.6

Run A5

The feed to Run A5 was Nebraska limestone. This limestone showed very little activity toward H_2S; only about 1% conversion to CaS occurred. However, the rate of attrition was 0.4%.

Runs A10 and A13

Run A10 was to be made with 1691 limestone to determine whether our results showing Nebraska limestone to be a poor acceptor were peculiar to that stone. A preliminary result was that the attrition rate was 0.9% of the feed rate, but the run was plagued with numerous operating difficulties and could not be brought to a successful conclusion.

Run A13 was made with 1691 limestone as a repeat of aborted Run A10. The attrition rate was acceptably low at 0.6% of the feed rate and H_2S removal was good. The regeneration of the stone did not appear to proceed as readily as with Canaan dolomite, i.e., compare Figures 46 and 40. With the Canaan dolomite (Figure 40), it took 13 cycles to sulfide the acceptor to 99% CaS, and upon regeneration, 13% of the CaS was removed. The corresponding figures for the 1691 stone (Figure 46) were 10 cycles and only 6% regeneration of the CaS.

Run termination was caused by inability to remove acceptor from the gas desulfurizer. Upon disassembly, the contents of the gas desulfurizer were found to be agglomerated in a single mass. In addition, difficulty in transferring acceptor between the vessels and the presence of +28 mesh agglomerates had been experienced during the entire run.

The agglomerates from the sulfur reactor were raspberries with a hard core of yellow material. The agglomerates were 50% soluble in cold, 0.5 N HCl.

The sample of 1691 limestone which we received had an unusually high level of impurities. The stone contained only 64 wt. % $CaCO_3$ and showed a 9.5% weight loss when heated at half-calcining conditions (1550°F, 1 atm. CO_2).

The good activity toward H_2S was probably due to the porosity resulting from the weight loss which occurred at half-calcining conditions. The 1691 behaved like a cross between a dolomite and a pure limestone. The agglomerates were probably caused by a low-melting liquid formed from the impurities, possibly in conjunction with CaS.

The 1691 was a rather unusual stone. It is doubtful that the results which were obtained would apply to ordinary limestones or dolomites.

G. Once-Through Operation

Runs A8 and A9

Two runs were made using once-through operation to provide a basis for cost comparisons with process variations using regeneration. Run conditions are listed in Table 51. Dolomite was fed in the raw condition; calcination of $MgCO_3$ was assumed to occur as soon as the solids hit the hot bed. The CO_2 of calcination is therefore not included in the calculated gas composition just above the bed. It is also excluded from the equilibrium calculation. Samples were taken after some four or more bed turnovers had occurred.

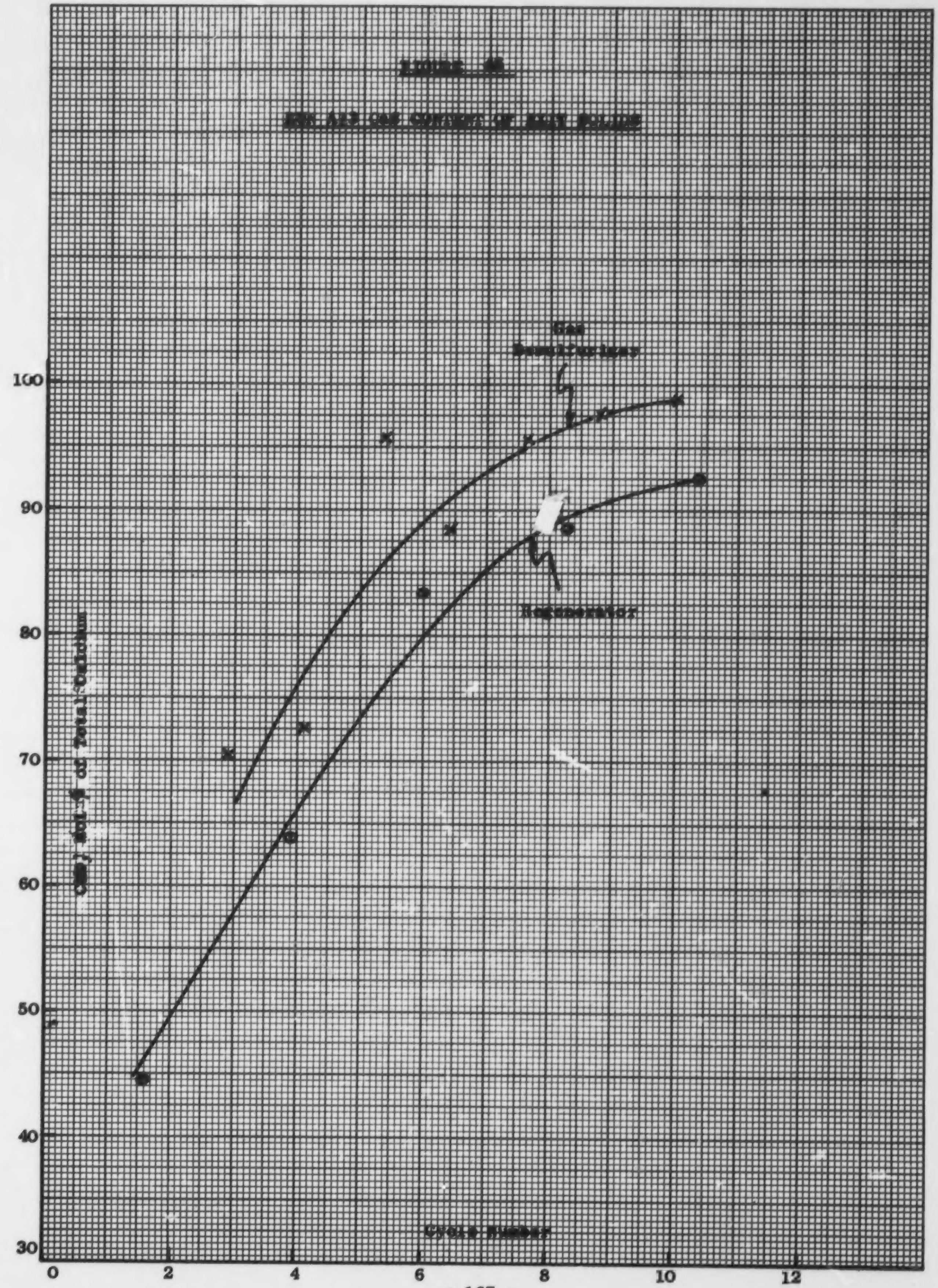

FIGURE [illegible]

[illegible] CONTENT OF EXIT SOLIDS

K+E 10 X 10 TO ½ INCH 46 1323
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

Table 31

Conditions and Results for Gas Desulfurizer - Once-Through Operation

System Pressure: 15 atm (206 psig)
System Temperature: 1600°F

Run Number	A8		A9	
Acceptor and Size Consist, Tyler Mesh	28 x 48 ← Tymochtee Dolomite →			
Feed Rate, lb/hr, Raw Stone	2.01		1.68	
Solids Residence Time, minutes	95		116	
Input, SCFH				
Recycle to Bed	160		160	
H_2S	2.8		2.8	
CO_2	46		46	
H_2	64		64	
H_2O	-		-	
N_2	82		82	
Purges (CO_2) to Bed	5		5	
Purges (N_2) above Bed	15		15	
Recycle, Acceptor Lift Gas, above Bed	71		71	
Output, SCFH				
Exit Gas Rate, SCFH (dry basis)	188		189	
Composition, Mol %				
H_2	17	(1)	17	(1)
CO	17		17.5	
CO_2	14		13	
N_2	52		53	
H_2S	.059		.16	
Outlet Gas, Top of Bed				
Composition, Mol %				
H_2O	9.4		9.7	
H_2	16.7		16.1	
CO	16		16.7	
CO_2	12.4(2)		11.6(2)	
N_2	45.4		45.7	
H_2S	.057		.153	
Flow Rate, SCFH, at Top of Bed	362		365	
Fluidizing Velocity, ft/sec	.52		.53	
Attrition, % of Feed Rate	1.3		.8	
Duration of Circulation with H_2S Feed, hrs	9.6		10.1	
Removal of Feed Sulfur	96		89	
Removal of Feed + Recycle Sulfur, %	93		81	
% H_2S in Outlet/Equilibrium % H_2S	1.7		4.6	
Conversion of Acceptor/Pass, mol %	89(3)		80(3)	

(1) Estimate.
(2) CO_2 of $MgCO_3$ calcination not included.
(3) Based on gas analysis. Assays on solids show 85% and 86% for A8 and A9 respectively.

Based on assays of the solids, the conversion was 85% in Run A8 and 95% in Run A9. However, H_2S removal was only 89% in Run A9 as compared to 96% in Run A8. The data show that once-through operation in the range of 85-90% solids conversion is feasible. The attrition rate using the raw stone feed was about 1% of the feed rate. The high conversion obtained was consistent with the results of Run A7.

H. "Refractory" CaS - Runs A16 and A17

Part of our solids assay procedure involved air oxidation of CaS by burning in an air-fluidized bed which is slowly heated from 1300-1600°F, and then held at temperature for 30 minutes. As originally set up, all of the CaS would be reacted to $CaSO_4$ or CaO. It was found that generally a portion of the CaS in reactor samples was resistant to oxidation, and this material was called refractory CaS. Although the reactions and reaction conditions in the regenerator and assay differ, the possibility that formation of refractory CaS would correlate with inactivity of CaS in the regeneration reaction was considered. At the end of Run A16, the level of refractory CaS was studied as a function of time at regenerator conditions. Run A17 was designed to examine the change in refractory CaS with time in the gas desulfurizer by sulfiding a batch of acceptor at simulated process conditions, turning off the H_2S feed, and then sampling from the vessel several times.

The results are given in Table 52. The data show that refractory CaS is converted slowly to ordinary CaS under regenerator conditions. There was no change in the refractory CaS under gas desulfurizer conditions.

It was found that regenerator performance does not correlate with refractory CaS as determined from our assay. At the end of Run A7, the refractory CaS from the regenerator was 48% and the CaS conversion per pass was 13%. In Run A16, the refractory CaS was 26% and the conversion of CaS was only 8%.

It seems that refractory CaS does not form from ordinary CaS, but rather is made when the CaS is first formed. One would speculate that inactive CaS differs morphologically from the active material giving rise either to diffusion limitations on a microcrystalline level or to a different adsorptive surface for reacting species. Build up of inactive CaS also may be responsible for poor kinetic results reported when batch cycle regeneration of CaS is carried out.(17)

A number of samples were sent to our analytical laboratory for sulfur analysis using a variation of the Eschka method as outlined in ASTM Method D-271. The results were in error on the low side. Oxidation of CaS to $CaSO_4$ is involved and not all of the sulfur was picked up.

J. Accuracy of H_2S Feed Rate - Sulfur Balance

We have not been able to properly close sulfur balances in this experimental system. In Run A9, for example, the sulfur balance based on the feed rate of solids and the H_2S content of inlet and outlet gas shows 80% molar conversion of $CaCO_3$ to CaS. The assay of the product shows 95% conversion of $CaCO_3$ to CaS. For cyclic operation, calculations become more uncertain because of the unsteady state nature of the inlet and outlet CaS concentrations, accumulation in the reactor and the exit gas composition. However, such balances also close ± 20%.

Our most accurate numbers are the measured exit gas concentrations and the solids assays. The most inaccurate number is the feed rate of liquid H_2S. Although it is not nearly as sensitive to temperature as is gas density, temperature variations can cause a 10% change in liquid density. Finally, it is known that H_2S can react with the reaction vessel.

The accuracy of solids assays was improved as our understanding of the behavior of inactive species improved. A revised H_2S feed system is under consideration, but could not be installed during this contract period.

K. Corrosion

At the start of the sulfur cycle studies, the gas desulfurizer vessel and internals were made of type 310 stainless steel. At the end of Run A1, the gas desulfurizer was found to have accumulated a blob of molten, yellow, metallic sulfides at the gas inlet line. Part of the inlet line was severely corroded and embrittled. A new coil and gas inlet line for the sulfur reactor were fabricated from type 446 stainless steel which is more resistant to a reducing atmosphere than type 310. The remainder of the internals were replaced with type 446 stainless steel during a shut down of Run A10. At that time, the reactor body showed scaling, but was replaced with type 310 since the type 446 stainless for the body was not on hand.

No corrosion problems were encountered in the regenerator which had both a body and internals made of 310 stainless steel.

L. Conclusions and Summary of Major Results

Attrition

The attrition rates for all stones tested are presented in Table 53. An attrition rate of 1% or less is desired, and only the Canaan dolomite was satisfactory. Limestones had good attrition rates, but the Nebraska stone was not active and the 1691 limestone agglomerated in the gas desulfurizer.

It is probable that many dolomites can be found which will have the requisite attrition resistance. There is some evidence that limestones are generically inactive toward H_2S.(15)

By using a strong, deactivated acceptor from previous OCR experiments, it was shown that the sulfur cycle under consideration does not intrinsically cause softening and attrition to occur.

Activity in the Gas Desulfurizer

All the natural dolomites showed good reactivity toward H_2S. Using only an 18-inch deep bed with gas residence times of 2 to 4 seconds, the exit H_2S concentration was only 2 to 3 times the calculated equilibrium value. Typically this activity was maintained with CaS loadings of 80% in the solid. Better results should be obtained in deeper, commercial sized units.

Tests with once-through operation showed that CaS loadings of 85-90 mol % are feasible.

Table 52

Change in "Refractory" CaS When Held at Reaction Conditions

Run No.	Material and Conditions	Holding Time, Hours	Mol %		
			$CaCO_3$	Total CaS	Refractory CaS
A16	Regenerator bed, 10.5 cycles, held at regenerator conditions.	0	11.7	88.3	25.5
		.5	13.1	86.9	23.3
		1	14.0	86.0	21.0
		2	14.6	85.6	18.6
		10	17.5	82.5	14.6
A17	Newly sulfided bed. Held at gas desulfurizer conditions.	0	56.0	44.0	6.3
		.5	58.7	41.3	5.1
		1.0	53.3	39.4	7.4
		4.0	58.3	41.7	5.3
A7	Regenerator bed, 12.9 cycles, held at regenerator conditions.	0	14.7	85.3	47.7
		2.0	24.1	75.9	35.7
A15	Regenerator Bed, 17.1 cycles	0	10.1	89.9	39.4

Table 53

Attrition Rate of Acceptors

Type of Stone	Origin	Attrition Rate, Wt % of Feed Rate
Dolomite	Plymouth Meeting, Pa.	9
↓	Tymochtee formation	5
	Buchanan, Va.	5
	Canaan, Conn.	0.8
Deactivated Dolomite	Cycling runs for OCR	0.2
Limestone	Nebraska	0.4
↓	BCR-1691	0.2

Regeneration, CaS → $CaCO_3$

The regeneration step has not gone to completion under the conditions employed. The CaS content of the acceptor builds up until it is 95 mol % or more. The CaS content then cycles between this upper limit and the CaS content of the regenerated stone. The best conversion observed was 13 absolute mol % in Run A7. The longest run was Run A15 which ran for 17 cycles. From cycle 8 to 17, the regeneration activity declined from 8 mol % per pass to 6 mol %.

It appears that as the acceptor is cycled, the CaS changes into an inactive form. The reaction times in the regenerator produce only marginal additional conversion to $CaCO_3$. Changing the temperature from 1300 to 1100°F did not improve the regeneration. Varying the steam/CO_2 ratio also yielded no improvement.

It is concluded that in a commercial process, the CaS would cycle between two high levels such as 90 and 75%. Sulfidation and regeneration would be 10 to 15% per cycle and a large number of cycles will be needed.

Toward the above end, one run has given 13% conversion in the regenerator per cycle, and another has demonstrated 17 cycles without serious loss of activity over the range of 8 to 17 cycles.

M. Future Work

Demonstration of Activity for a Large Number of Cycles

It has been concluded that the acceptor could be cycled at 13% conversion per pass without losing its ability to remove H_2S in the gas desulfurizer. A demonstration of this conclusion is needed. It has not been actually shown that high removal efficiency can be obtained with a cycled stone which is cycled from about 77% to 90% conversion. In our runs so far, H_2S breakthrough in the gas desulfurizer occurred because of 20% per pass of H_2S being fed. Also, at the 13% conversion per pass, only about 12 cycles were actually demonstrated.

Squires Reaction - Approach to Equilibrium

The work done to date simulated only the bottom of the regenerator since the maximum H_2S concentration was about 1% (wet basis) compared to about 4.5% at equilibrium. The process design assumes about 3.6% H_2S or 87% approach, and this has yet to be demonstrated.

The kinetics of the reaction remain to be further investigated. Specifically, the effect of the H_2O/CO_2 ratio and the effect of temperature as they affect rate of reaction, approach to equilibrium and the regenerability of the stone require more work.

Attrition

Of the four dolomite acceptors studied, three had excessive rates of attrition. It has to be established that satisfactory acceptors can be obtained in areas close to projected gasification plant sites. Alternately, conditions or treatments must be determined to render other acceptors more resistant to attrition.

Effect of Particle Diameter

The studies to date were restricted to 28 x 48 Tyler mesh particles. It remains to be determined how the larger particles, which would be used in the scaled up process, would behave.

Blocked Out Operation

In order to unequivically define the relationship of CaS content to number of cycles, it will be necessary to operate the gas desulfurizer-regenerator combination so that all of the acceptor is run through before the next cycle is started. This will necessitate running with a large starting batch of feed and discarding the start-up and shut-down beds as the run proceeds.

X. CARBON BURN-UP CELL AND GASIFIER DEMONSTRATION RUNS

A. Carbon Burn-Up Cell Study

1. Introduction

The CBC concept provides for preheat of the steam-air mixture for the gasifier by combustion of the gasifier residue char.

Combustion of char at high oxygen partial pressures poses the threat of localized hot spots and consequent ash slagging. The incoming process steam and air to the CBC are relatively cold, and thus provide a heat sink which should prevent ash slagging.

The experimental work presented here was designed to demonstrate the limiting operating conditions in the CBC under which efficient utilization of the feed char and lack of ash slagging are simultaneously obtained.

Combustion was carried out in inert beds of dead burned dolomite or silica sand in the 3-inch I.D. reactor used as the gas desulfurizer in the sulfur cycle study. The bed height was 18 inches. A flow diagram of the system is shown in Figure 47.

Run conditions were chosen within the framework established by the process heat and material balance calculations.

Eight runs were made using pregasified Pittsburgh Seam coal char as fuel at inlet oxygen pressures of 2.2 atmospheres. Conditions and results are shown in Table 54. Table 31 gives the descriptions of the runs not specifically mentioned in Table 54. Compositions of the char feedstocks are shown in Table 55.

These feedstocks were partially gasified Pittsburgh Seam coal char, used to simulate the actual gasifier product which is the feed to the carbon burn-up cell.

2. Runs CBC-1 through CBC-4

These runs were made with dead burned dolomite as the inert bed material. They explored the effect of bed expansion on bed temperature gradient and on ash slagging.

Run CBC-2, over a period of about 20 hours at 1880°F and 55% bed expansion, gave no evidence of ash slagging but did show a moderately high temperature gradient. The inlet gas flow rate then was decreased to give a bed expansion of 41%. After about 20 hours of additional operation at this latter condition, the temperature at the bottom of the bed increased suddenly to 1950°F and the run was ended. Inspection of the reactor showed that slag, amounting to about 1% of the total ash fed, had formed at the bottom.

Run CBC-3, made at the slightly lower temperature of 1850°F showed that, at least for 13 hours, no slagging occurs at the low bed expansion of 30%. However, a large temperature gradient existed.

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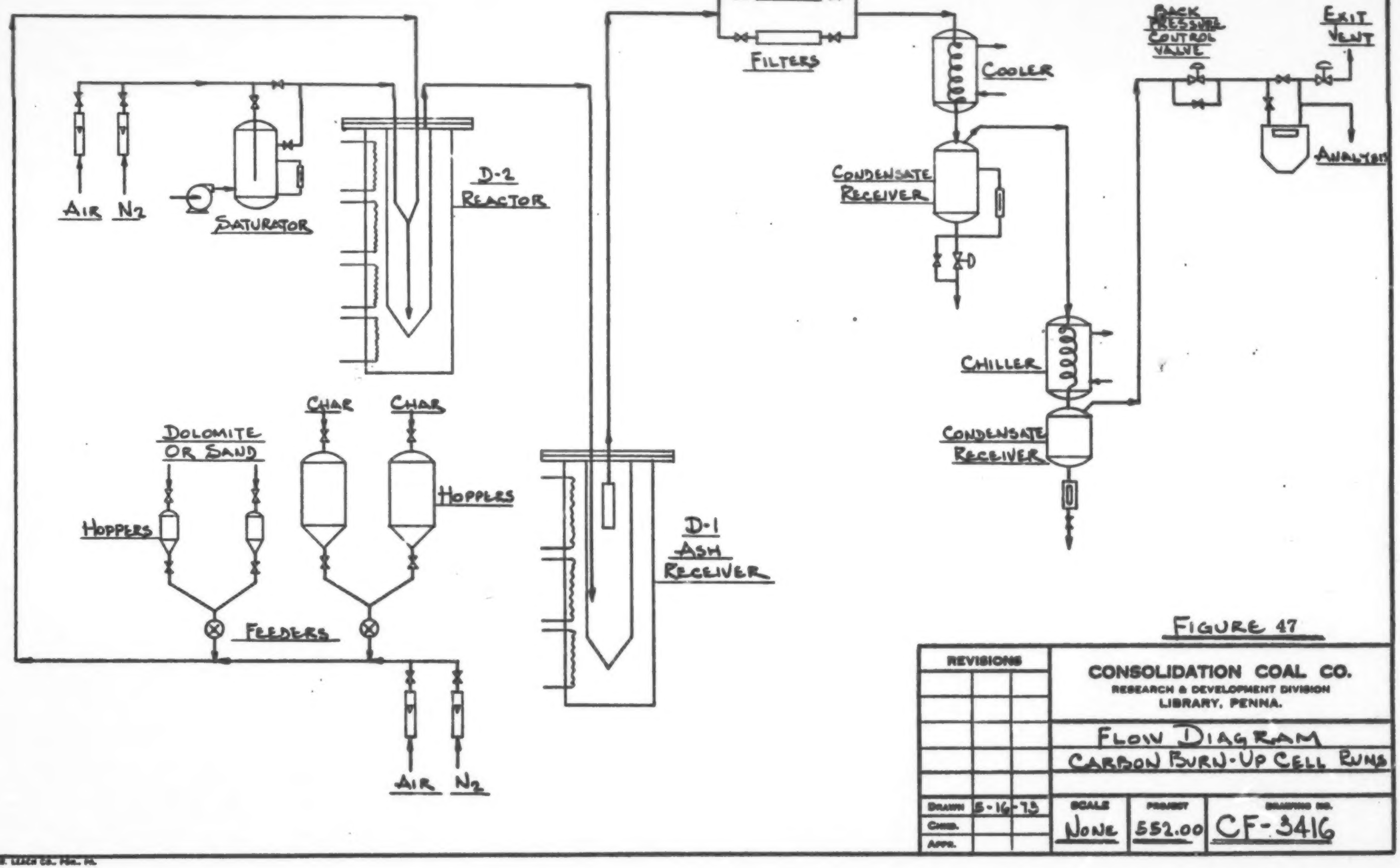

AIR
N2
SATURATOR
D-2
REACTOR
DOLOMITE OR SAND
HOPPERS
CHAR
CHAR
HOPPERS
FEEDERS
AIR
N2
D-1
ASH
RECEIVER
FILTERS
COOLER
CONDENSATE
RECEIVER
CHILLER
CONDENSATE
RECEIVER
BACK PRESSURE CONTROL VALVE
EXIT
VENT
ANALYSIS

FIGURE 47

REVISIONS		

CONSOLIDATION COAL CO.
RESEARCH & DEVELOPMENT DIVISION
LIBRARY, PENNA.

FLOW DIAGRAM
CARBON BURN-UP CELL RUNS

			SCALE	PROJECT	DRAWING NO.
DRAWN	5-16-73		NONE	552.00	CF-3416
CHKD.					
APPD.					

Table 54

Conditions and Results for Carbon Burn-up Cell Runs

Vessel I.D. 3" - Bed Height 18"
System Pressure: 15 atm. (206 psig)

Run	CBC-2		CBC-3	CBC-4	CBC-5				CBC-6
Bed Material	Dead Burned Dolomite		Dead Burned Dolomite	Dead Burned Dolomite	Silica Sand				Silica Sand
Size, Tyler Mesh	35 x 48		28 x 35	35 x 48	28 x 35				28 x 65
Temperature	1880		1850	1850	1700	1750	1800	1850	1850-1900
Fuel Char	K2A-K7A Product		K2A-K7A Product	K2A-K7A Product	D12 Product				D12 Product
Input, SCFH									
Steam	132	110	158	167	← 165 →				169
Air									
Lift Gas	70	70	70	70	← 70 →				70
Fluidizing Gas	279	220	350	350	← 350 →				350
Purges (N_2)									
To Bed	5	5	5	5	← 5 →				5
Above Bed	20	20	20	20	← 20 →				20
Fuel Char Feed Rate, lb/hr	1.14	.997	1.46	1.39	← 1.23 →				1.41
Output, Top of Bed, Mol %									
Steam	27.3	27.3	27.2	28.3	← 28.1 →				28.6
O_2	9.0	8.9	8.7	8.9	← 9.5 →				8.6
N_2	57.7	57.6	57.8	56.9	← 57.0 →				56.6
CO_2	6.0	6.2	6.3	5.9	← 5.4 →				6.2
Flow Rate, SCFH at Top of Bed	487	406	584	593	← 591 →				595
Ash, lb/hr	.217	.190	.278	.265	← .191 →				.226
Exit Gas Composition, Mol %, dry basis(1)									
O_2	11.8	11.4	11.5	11.9	← 12.6 →				11.5
N_2	80.4	80.7	80.2	80.2	← 80.2 →				80.2
CO_2	7.8	7.9	8.3	7.9	← 7.2 →				8.3
Fluidizing Velocity, Top of Bed, ft/sec	.79	.66	.94	.95	.89	.91	.93	.94	.98
O_2 Partial Pressure, atm									
Inlet	2.26	2.26	2.27	2.23	← 2.24 →				2.23
Outlet, Top of Bed	1.36	1.33	1.31	1.34	← 1.42 →				1.29
Bed Temperature Gradient, °F(2)	57	117	124	20	17	5	7	38	22
Run Duration, hours	21	20	13	31	← 13.5 →				25
% Bed Expansion(3)	55	41	30	75	48	52	53	54	67

(1) Includes all N_2 purges.

(2) Difference between bottom of bed and top of bed.

(3) Percent bed expansion above incipiently fluidized bed height, 100% expansion is twice the incipient height.

Table 55

Compositions of Char Feedstocks

Used in Run	CBC-1 → CBC-4	CBC-5 → CBC-8
Produced in Run	K2A → K7A	D12
Hydrogen, Wt % (dry basis)	.50	.46
Carbon	78.84	81.11
Nitrogen	.54	.75
Oxygen (by difference)	.37	-.18
Sulfur	.47	1.70
Ash	14.28	16.16
Sulfide Sulfur		.85

In Run CBC-4, the bed expansion was increased to 75% at 1850°F by substitution of 35 x 48 mesh dead burned dolomite for the 28 x 35 mesh stone used in CBC-3. The temperature gradient decreased to only 70°F. No slag had formed after 31 hours.

The bed of the dead burned dolomite proved to be reactive toward SO_2 formed during combustion of the fuel char. Nearly quantitative pickup occurred with the result that the particle size and density of the bed continually changed during the runs. To prevent changes in fluidizing characteristics of the bed, silica sand was used as bed material in place of dolomite in Runs CBC-5 through CBC-8.

3. Runs CBC-5 through CBC-8

The behavior of silica sand as inert bed material was checked in Run CBC-5, and combustion characteristics at the low end of the envisioned temperature range were determined. Operation was smooth at all conditions, with no ash slagging and low or moderate temperature gradients. Inspection of the product ash showed that the char carbon was completely consumed, even at 1700°F.

In Run CBC-8 the bed temperature was increased to 1900°F at a bed expansion of 67%. After 25 hours, no slag had formed and the temperature gradient was moderate throughout. Typical temperature profiles are shown in Figure 27.

4. Ash Properties

The product ash from all the runs had no detectable carbon content. Some properties of the Loveridge char ash are shown in Table 56. Also shown are the size consist and ash particle density for Run CBC-5. The product ash from each of the other runs was nearly identical. The fuel char feedstock to the carbon burn-up cell for all runs was substantially 100% +100 mesh. As Table 56 shows, the product ash is nearly all -100 mesh.

5. Conclusions

The experimental work shows that the carbon burn-up cell will be trouble-free. Complete carbon consumption occurs at temperatures as low as 1700°F within a bed height of 20 inches. Freedom from ash slagging and a moderate temperature gradient has been demonstrated at 1900°F. What is required is sufficient mixing of the inert bed particles. Our data show that 60-70% bed expansion is sufficient to provide the necessary mixing.

B. Gasifier Demonstration Runs

1. Introduction

At the bottom of the gasifier where the preheated air and steam from the carbon burn-up cell first contact the incoming pretreated coal feedstock, the possibility exists that ash slagging will occur or that ash-derived deposits will form.

For the experimental program, the char feedstock was pretreated at 1200°F to avoid caking problems. Thus, it simulated the product from the Seeded Coal Process.

Table 56

Ash Properties

Ash Composition, Sulfur-Free Basis	
Al_2O_3, Wt %	24.3
SiO_2	44.1
Fe_2O_3	17.6
CaO	8.7
MgO	1.8
Na_2O	.9
K_2O	1.4
TiO_2	.8
P_2O_5	.4

ASTM Ash Fusion, Oxidizing	°F
Initial	2300
Softening	2380
Hemispheric	2420
Fluid	2600

Product Ash, Run CBC-5

Size, Tyler Mesh, Wt %	
+65	.0
65 x 100	4.7
100 x 200	20.1
-200	75.2

Particle Density, lb/ft^3* 100 (100 x 200 Mesh Fraction)

* Measured in mercury at one atmosphere.

The runs reported here were carried out in the vessel used for regeneration of the sulfur-laden acceptor. The bed diameter was 4-inches and bed height 48 inches.

2. Results

Three runs were made at process conditions where the steam, CO_2, and O_2 partial pressures were the same as in the effluent from the carbon burn-up cell in order to simulate conditions at the bottom of the process gasifier. The purpose of the runs was to determine whether ash slagging or wall deposits occur. The feedstock was char prepared from Loveridge Mine coal (Pittsburgh Seam).

Run D11 was made at 1725°F and there was no evidence of ash slagging or of wall deposits. Run conditions and results are shown in Table 57. Feed and product char compositions are given in Table 58.

To help define the temperature limit for the onset of ash slagging, Run D12 was attempted at 1775°F with the 1200°F pretreated feedstock. A large coke-like deposit formed quickly. Although the formation of coke from a material which had been exposed previously to 1200°F was considered unlikely, another batch of feedstock was prepared at 1400°F to eliminate any possibility of coke formation.

Run D13 was made at 1775°F with the 1400°F pretreated feedstock. After about six hours of char feeding, the temperature at the bottom of the fluidized bed increased rapidly to 2000°F, and the run was ended. Inspection of the vessel showed a massive deposit similar in appearance to that of the previous run. A small amount of slagged ash was present at the bottom of the vessel. Slagging clearly was caused by continued encroachment of the deposit into the zone where the incoming oxygen and char met. The normal mixing pattern of the fluidized bed thereby was altered, allowing a hot spot to develop.

Conditions and results for Run D13 are shown in Tables 57 and 58. The material balance period for the run was made before the hot spot developed.

The superficial appearance of the deposits from both 1775°F runs was misleading. Neither deposit was coke, as shown by their carbon content of one weight percent. Chemical analysis of the deposits showed that their composition was nearly identical with that of the char ash shown in Table 56. Thus, the deposits were built up by mild slagging of the ash.

3. Conclusions

Complete operability has been demonstrated at 1725°F. In contrast with the carbon burn-up cell runs, in which the same char ash was present, sintering or incipient slagging caused a buildup of ash at the bottom of the reactor at 1775°F. The carbon burn-up cell runs were made, in general, at considerably higher temperatures and at strongly oxidizing conditions.

Ash fusion temperatures can be altered drastically under reducing conditions such as exist in the gasifier. Possibly, operation at 1775°F would be successful if better mixing of the char were achieved though the use of higher bed expansions and fluidizing velocities. Existing equipment limitations preclude higher fluidizing velocities than were used in Runs D12 and D13.

Table 57

Conditions and Results for Demonstration Runs

System Pressure: 15 atm (206 psig)
Feedstock: Pretreated Loveridge Char (Pgh. Seam)
Vessel ID - 4" - Bed Height 48"

Run Number	D11	D13
Feedstock Pretreatment Temperature, °F	1200	1400
Run Temperature, °F	1725	1775
Input		
Steam, SCFH	98	96
CO_2	23	21
Air	134	158
Lift Gas, N_2	91	76
Purges (N_2) to bed	10	10
Purges (N_2) above bed	15	15
Char Feed Rate, lb/hr	6.06	7.53
Output		
Exit Gas Rate, SCFH (dry basis)	377	406
Composition, Mol %		
H_2	13.94	14.47
CH_4	.56	.64
CO	14.97	19.12
CO_2	11.55	10.06
H_2S	.24	.22
N_2	58.98	55.49
Outlet Gas, top of bed		
Composition, mol %		
H_2O	14.38	10.93
H_2	12.44	13.39
CH_4	.50	.59
CO	13.36	17.69
CO_2	10.31	9.32
H_2S	.21	.20
N_2	48.80	47.89
Flow Rate, SCFH at top of bed	422	439
Fluidizing Velocity, ft/sec	0.38	0.40
Product Char, lb/hr	3.32	4.06
Duration of Char Feeding, hr	12.0	6.2
Bed Weight, lb	7.95	7.93
Carbon Gasified, lb/hr	2.45	3.09
% Carbon Burnoff(1)	48.4	49.9
% Steam Conversion	38.0	50.0

(1) $$\frac{100\ (\text{lb/hr net carbon in exit gas})}{(\text{lb/hr carbon in with char})}$$

Table 58

Analyses of Char Feed and Products for Demonstration Runs

Run Number	D11		D13	
	Feed	Product	Feed	Product
Hydrogen, Wt %, (dry basis)	1.59	.48	1.08	.41
Carbon	80.58	77.45	82.30	80.37
Nitrogen	1.32	.73	1.60	.76
Oxygen (by difference)	2.27	-.76	.33	.46
Sulfur	2.09	1.62	2.13	1.62
Ash	12.15	20.48	12.56	16.38*

Run D11 Product

Size, Tyler Mesh	Wt %	Particle Density, lb/ft^3
28 x 35	12.4	75.5
35 x 48	32.9	70.9
48 x 65	29.5	71.1
65 x 100	20.4	70.1
-100	4.8	

* Ash content is low because of deposit which remained in the gasifier.

XI. LIQUID-PHASE CLAUS PROCESS

A. Introduction

The composition of the gas leaving the regenerator as projected in the feasibility study in the Annual Report(1) contained about 4% H_2S, 48% H_2O, and 48% CO_2. Elemental sulfur is recovered by contacting this gas with sulfurous acid at the saturation temperature, ca. 325°F. The reaction taking place is:

$$2\ H_2S + H_2SO_3 = 3\ S + 3\ H_2O.$$

Elemental sulfur is recovered as a liquid.

Since nothing was known of the kinetics of the liquid-phase Claus reaction, conditions were chosen to match the gas concentrations and vapor liquid ratio given in the Annual Report. Flow rates were chosen to give the same vapor retention time, and the feed rate per unit volume of reactor space was the same as projected in the Annual Report. A total of eleven runs were made. The data are summarized in four tables as given below:

Table 59 - Results and Conditions for Liquid-Phase Claus Reaction
Table 60 - Sulfur Balances for Liquid-Phase Claus Reaction
Table 61 - Yields of Elemental Sulfur
Table 62 - Analysis of Claus Product Liquor

B. Once-Through Runs

Runs C1 and C2

Run C1 was made at 320°F. The outlet SO_2 concentration was near zero for the entire run; the H_2S concentration was not determined. Sulfur could be seen in the column, but none could be collected at the bottom. The condensate was bright yellow, the color of Wackenroder's solution of sulfur together with soluble sulfur byproducts. Analysis of the product solvent showed only 0.06% sulfur. The run ended when the exit line plugged.

The run indicated that sulfur can be readily produced with little by-product formation under process conditions. There were insufficient data for a sulfur balance.

Run C2 was a repeat of C1. The same observations with respect to sulfur collection and sulfur content of the condensate and product solvent were made. Analysis of the exit gas gave 3.4% H_2S and 0.2% SO_2. H_2S and SO_2 which had not reacted in the column were absorbed in the condensed steam to form Wackenroder's solution. The ratio of H_2S to SO_2 in the dry exit gas indicates that SO_2 was preferentially absorbed by the cooled condensate. Sufficient data were on hand to make a crude sulfur balance as shown in Table 60. The balance showed 40% conversion of the feed to elemental sulfur. However, after 2-1/2 hours of operation, only 25% of one hour's feed was collected as elemental sulfur. Liquid sulfur was visible in the column and a wash with hot toluene yielded some additional sulfur.

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Table 52

Results and Conditions for Liquid-Phase Claus Reaction

System Pressure: 15 atm (208 psig)
Packing: 3 mm glass beads

Run Number	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
Temperature, °F	320	320	310	310	310	310	310	310	310	310	310
Absorbent Liquid	← 6% SO_2 in H_2O →			1.68% SO_2 in H_2O	10% $Na_2S_2O_3$ in H_2O	Recycle Solvent Liquor			(4)	(4)	(4)
Packing Volume, cc	415	415	415	415	415	415	208	101	↓	↓	↓
Liquid Feed Rate, lb/hr	1.31	1.38	1.45	5.38	1.57	1.30	1.42	1.59	↓	↓	↓
Liquid Feed Rate, lb/hr-ft²	403	424	445	1650	480	400	430	490	↓	↓	↓
Gas Feed Rate, SCFH	24.1	24.1	26.2	28.5	29.1	28.8	29.5	29.5	29.1	29.7	28.6
Gas Feed Rate, SCF/hr-ft²	7400	7400	8050	8740	8930	8840	9060	9060	8940	9110	8770
Inlet Gas Composition, Mol %											
H_2O	38.8	38.8	34.0	35.2	35.1	35.4	34.5	34.5	32.8	34.3	34.6
CO_2	54.7	56.7	61.9	61.0	59.3	59.0	59.9	59.9	61.6	64.0	64.6
H_2S	4.5	4.5	4.1	3.8	3.74	3.77	3.68	3.68	3.73	1.151	.540
SO_2	0	0	0	0	1.88	1.88	1.84	1.84	1.86	.376	.370
Outlet											
Liquid Product, lb/hr	1.2	1.2	1.2	5.08	1.2	1.33	1.57	1.60	(4)	(4)	(4)
Weight % S	.06	.11	.07	.06	2.99	.11	.03	.04	.06	.03	.01
"Condensate", lb/hr	.57	.46	.46	.58	.41	.43	.49	.53	.44	.48	.45
Weight % S	ca. .4	3.3	2.8	2.7	1.74	3.9	4.0	7.4	5.6	.95	.50
Product Sulfur, lb/hr	N.D.	.05(1)	.057	.062	.084	.090	.070	.058	.092	.083	.0083
Exit Gas Rate, SCFH, (dry basis)	14.1(2)	14.1(2)	16.5(2)	17.6(2)	17.4(2)	17.2	18.2	18.0	18.2	19.2	18.5
H_2S, Mol %	N.D.	3.4	1.9	1.5	1.4	1.2	2.56	1.11	1.30	.85	.47
SO_2, Mol %	0.0	0.2	.1	.06	.03	0.1	.06	.40	.62	.33	.13
% Conversion of Feed Sulfur to Elemental Sulfur(3)	N.D.	41(1)	42	46.0	62.2	66.7	51.7	43.1	68.5	54.8	43.3

(1) Approximate value, determined by difference.
(2) Maximum value, assumes no CO_2 loss due to solution in product liquids.
(3) In column only, excludes Wackenroder sulfur in condenser, sulfur in recycle liquor, or thiosulfate in liquid feed.
(4) Runs C9, C10 and C11 were made with a single batch of water filling one half of the column. No packing was used.

N.D. - Not determined.

Table 60

Sulfur Balances for Liquid Phase Claus Reaction

All Weights on an Hourly Basis

Run Number	C2		C3		C4		C5		C6	
	Grams	Percent	Grams	Percent	Grams	Percent	Grams	Percent	Grams	Percent
Feed Sulfur										
As H_2S	40.8	68.5	40.8	67.3	40.8	66.6	40.8	51.2	40.8	66.0
As SO_2	18.8	31.5	19.7	32.5	20.5	33.4	20.6	25.8	20.4	23.0
As $S_2O_3^{=}$	--	--	--	--	--	--	18.3	23.0	--	--
In Recycle Liquor	--	--	--	--	--	--	--	--	0.65	1.0
Exit Sulfur										
In Liquid Product	0.6	1	0.4	0.7	1.4	2.3	15.7	19.7	0.67	1.1
In Condensate	6.8	11	5.9	9.7	7.2	11.7	3.3	4.1	8.4	13.6
In Exit Gas	19.1	32	12.4	21	10.6	17.3	9.2	11.5	7.6	12.3
Elemental Sulfur Product	24.2(1)	41	25.7	42	28.1	45.9	38.3	48.0	40.9	66.1
Losses and Accumulation	8.9(2)	15	16.3	27	14.0	22.9	13.3	16.7	4.3	6.9

Run Number	C7		C8		C9		C10		C11	
	Grams	Percent	Grams	Percent	Grams	Percent	Grams	Percent	Grams	Percent
Feed Sulfur										
As H_2S	40.8	66.5	40.8	66.3	40.8	66.7	12.86	66.7	5.81	66.7
As SO_2	20.4	33.3	20.4	33.2	20.4	33.3	6.43	33.3	2.90	33.3
In Recycle Liquor	.13	0.2	0.3	0.5	--	--	--	--	--	--
Exit Sulfur										
In Liquid Product	.14	.23	0.3	0.5	--	--	--	--	--	--
In Condensate	8.9	14.5	17.8	28.9	11.1	18.1	2.08	10.8	1.02	11.7
In Exit Gas	17.9	29.2	10.2	16.6	9.5	15.6	7.73	40.1	4.13	47.4
Elemental Sulfur Product	31.7	51.7	26.4	42.9	41.9	68.5	10.58	54.8	3.78	43.4
Losses and Accumulation(3)	2.6	4.3	6.8	11.0	(-1.4)	(-2.2)	(-1.1)	(-5.7)	(-.21)	(-2.5)

(1) By difference.
(2) Estimated as 15% of feed.
(3) A negative number indicates the material balance exceeds 100%.

Table 61

Yields of Elemental Sulfur

Run No.	Run Time, hours	Yield of Elemental Sulfur, % of $SO_2 + H_2S$ Feed	Average Sulfur Yield After 2 Hours Lining Out Period, %
C3	1	0	42.4
	2	12.7	
	3	35.6	
	4.08	49.2	
C4	1.5	0	45.9
	2.5	43.2	
	3.5	39.3	
	4.5	51.5	
	5.5	44.0	
	6.5	48.9	
C5	.5	42.0	62.3
	1.5	62.0	
	2.5	62.3	
C6	1	0.5	66.7
	2	31.8	
	3	62.5	
	4	63.0	
	5	63.9	
	6	71.0	
	7	76.9	
	7.9	62.8	
C7	1	10.0	51.7
	2	39.0	
	3	54.2	
	4	58.7	
	5	47.9	
	6	47.2	
	6.2	50.3	

Table 61 (Cont'd.)

Yields of Elemental Sulfur

Run No.	Run Time, hours	Yield of Elemental Sulfur, % of SO_2 + H_2S Feed	Average Sulfur Yield After 2 Hours Lining Out Period, %
C8	1	7.7	
	2	17.6	
	3	39.4	
	4	41.8	43.1
	5	48.4	
	6	37.7	
	6.7	48.0	
C9	1	43.6	
	2	60.3	
	3	71.2	68.5
	4	67.5	
	5	69.9	
	5.5	65.4	
C10	2	50.8	
	3	53.4	
	4	54.4	54.8
	5	60.6	
	5.5	50.8	
C11	1	0.0	
	2	8.0	
	3	52.8	43.3
	4	34.4	
	5	41.3	
	6	44.8	

Table 62

Analysis of Claus Product Liquor

Run No.	Approximate Cycle No.(1)	pH	Total S, Weight %	S as SO_4, Weight %	S via Iodine(2) Titration, Wt %
C1	1	2.3	.06	.04	-
C2	1	2.5	.11	.04	-
	1	2.2	.11	-	-
	1	2.4	.04	-	-
C3	1	2.0	.10	-	-
	1	1.9	.08	-	-
	1	2.0	.07	.06	--
C4	1	2.1	.05	.04	-
	1	2.1	.02	.04	-
	1	2.1	.06	.04	-
C5	1	3.7	2.85	.81	-
	1	3.8	2.80	.75	-
	1	3.8	2.99	.68	-
C6	1	2.7	.03	.01	.03
	2	3.0	.13	.03	-
	3	2.9	.09	-	-
	4	2.8	.10	.03	.03
	5	2.8	.11	-	-
	6	2.8	.09	.04	.03
C7	1	2.5	.02	.01	-
	2	2.1	.04	-	-
	3	2.2	.04	.02	-
	4	2.5	.02	-	-
	5	2.4	.01	.01	-
C8	1	2.5	.02	.01	-
	2	2.3	.04	-	-
	3	2.2	.06	.02	-
	4	2.3	.03	-	-
	5	2.1	.04	-	-
	6	2.1	.04	.04	-
C9	(3)	2.1	.06	.03	.02
C10	(3)	2.5	.03	.02	-
C11	(3)	2.8	.01	.01	0.0

(1) Runs C1-C5 were not cyclic. Several analyses from once-through operation are given.

(2) Calculated as if $S_2O_3^=$ were being detected.

(3) Runs C9, C10 and C11 did not involve cyclical operations. The analysis given is for liquid withdrawn at the end of the run.

Run C3

At 320°F the viscosity of sulfur is 23 cp as opposed to 7 cp at 310°F. Run C3 was made at 310°F to see whether this would improve sulfur removal from the column. During the third hour of operation, elemental sulfur equivalent to 42% of the feed sulfur was obtained. Results are detailed in Tables 59 through 62.

Run C4

Run C4 was made at about four times the liquid throughput rate of Run C3; the gas rate was constant. It was anticipated that the higher liquid rate would increase holdup in the column. The increased liquid volume available for reaction should then have increased the conversion.

Reference to Table 61 shows that the average sulfur yield increased only 3.5% absolute. Assuming the dynamic liquid holdup to be proportional to the one-third power of the liquid flow rate,(18) a 3.7-fold increase in flow would produce a 55% increase in dynamic holdup. However, if the static liquid holdup were a large fraction of the total, this would explain the small response to the change in flow rate.

Run C5

Run C5 was made with 10 wt. % sodium thiosulfate (anhydrous) added to water. Sulfur dioxide was fed mixed with CO_2 as was the H_2S. This method is equivalent to feeding an SO_2-H_2O solution, since essentially all the SO_2 flashes from the SO_2-H_2O solution as the process temperature is approached.

According to previous work at ambient temperature,(19) thiosulfate is supposed to enhance the reaction. Conversion of sulfur based on H_2S and SO_2 feed was 62%. Although this represents an improvement over the previous runs, the improvement was not as dramatic as had been hoped for. In addition, about one-fifth of the feed thiosulfate ended up as sulfate at run conditions, and the sulfur balance showed another 14% of the feed thiosulfate apparently ended up as sulfur which added 4% to the conversion of H_2S and SO_2. The analyses of several product samples are given in Table 62.

C. Recycle of Product Liquor

Runs C6 to C8

These runs were made with SO_2 and H_2S entering the gas feed. Liquid product was collected, filtered of sulfur fines and returned to the feed pots. Samples were taken periodically; a cycle was completed in about 1.4 hours. Run C7 was carried out with half of the column packing removed, and Run C8 was carried out with three-fourths of the column packing removed.

In Run C6 an average conversion of 66.7% was obtained. This was the best result yet obtained in the column. The most comparable run, C3, showed only 42.4% average conversion. The major difference was the use of recycle liquor in Run C6. These observations indicate the build up of a component in the recycle liquid which reaches a steady-state concentration or level of activity after a few cycles.

Reference to Table 61 and Figure 48, shows that there was no trend in sulfur yield with cycling after the initial two hours of operation. Runs C6 to C8 ran for about six cycles. The lab setup was not equipped to run for many more cycles than this. Table 62 shows no trend in pH or sulfur content of the product liquor.

All the runs made without additives showed a pH of 2 to 3 in the product liquor. Apparently, this acidity was quickly established and remained constant. The product of Run C4 because of high throughput, saw the least reaction per unit liquid, and the pH was 2.1. The product of Run C6 went through the unit six times and the pH was 2.8.

All liquor products showed residual sulfur contents between 0.03 and 0.11 wt. % sulfur. A significant fraction of this was analyzed to be the sulfate form as can be seen from Table 62. The product liquor was also titrated with iodine, and the results of these titrations are given in Table 62. Since a number of sulfurous compounds can be detected via this method, it is not certain which species is actually present. The analysis merely shows the presence of a sulfur-bearing compound other than sulfate. It is also noted that the low concentrations involved preclude a high degree of accuracy at this time.

For runs C6 to C8, the conversion to sulfur is plotted versus the fraction of the column containing packing in Figure 49. Allowing for scatter, the data could fit either a first or second order system. The first order dependency can exist in a diffusion controlled or reaction rate controlled regime. Second order dependence is consistent with reaction control mechanisms. If the system were reaction rate controlled, increasing the liquid volume would increase conversion.

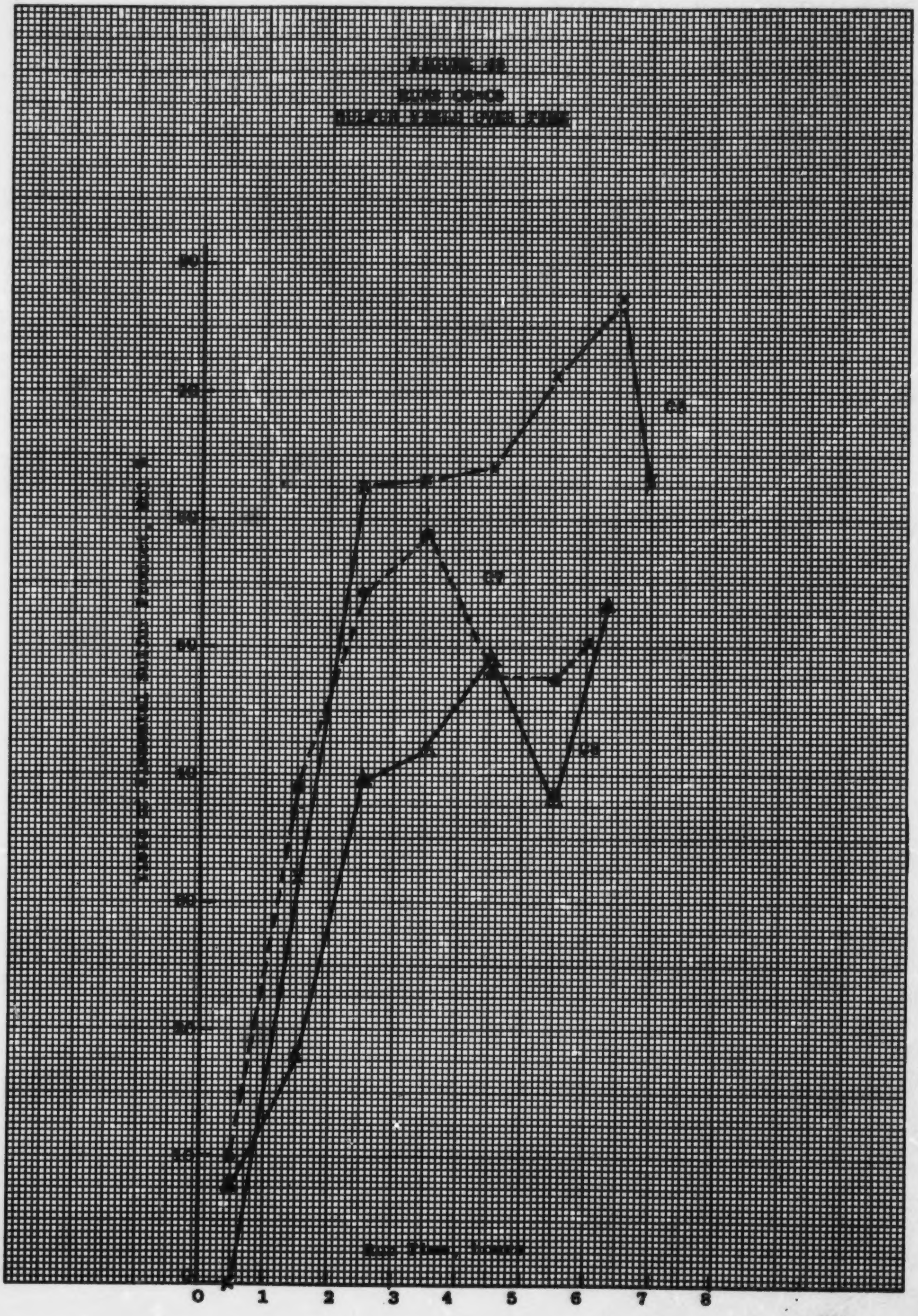
D. Batch Liquid Operations

Runs C9 to C11

Runs C9 through C11 were made with no packing and the column half filled with liquid, thereby increasing the volume of liquid per unit volume of reactor. The system was repiped so that gas entered through a sparger at the bottom and was withdrawn overhead. There was no liquid circulation; sulfur was withdrawn from the bottom of the column.

The average conversion in Run C9 was 68.5%. This was the highest conversion yet observed and it was obtained with only one half the column volume. The result may be compared with that of Run C7 when the column was 50% packed and the conversion was 51.7%.

Runs C10 and C11 were made at decreasing inlet gas concentrations. The inlet of C10 was the calculated outlet gas composition of C9, and the inlet of C11 was the outlet of C10. For example, the H_2S concentration leaving the column in Run C9 was (wet basis): $3.73 \times (1 - 0.685) = 1.175\%$. The inlet gas for Run C10 was 1.15%. Thus, a single long column was simulated by taking three reaction sections. Combination of the results gives 86% conversion for 100% of column volume (68.5 + .3 5 x 54.8) and 92% conversion for 150% of column volume. Since the gas throughput per unit volume of column and the gas concentration both match the process flow sheet, it is concluded that the column size listed in the Annual Report(1) and in this report is in reasonable concurrence with experimental results.

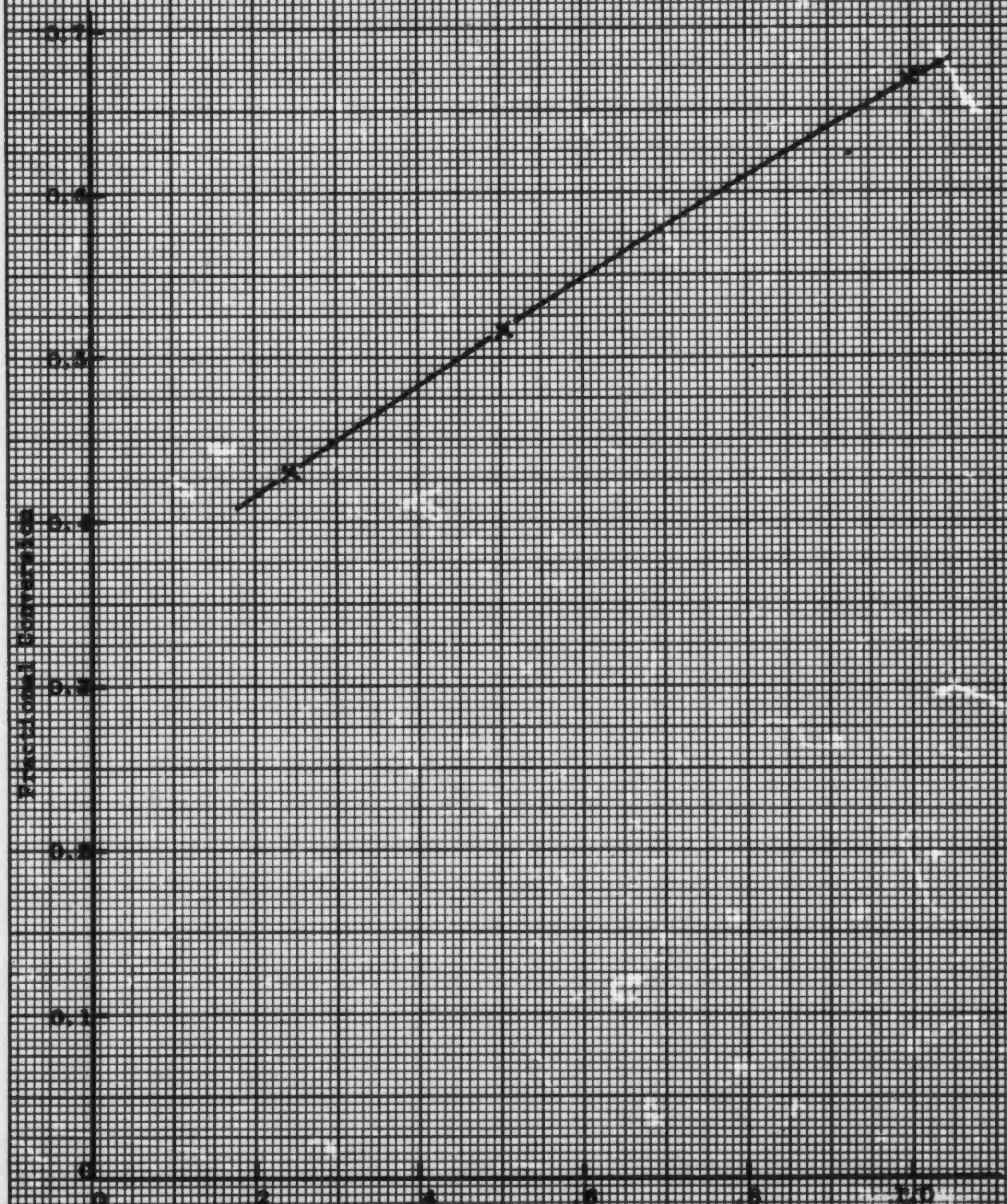


K+E 10 X 10 TO ½ INCH 46 1323
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

FIGURE 49

Runs C8-C5

Conversion vs Fraction of Column Containing Packing



K+E 10 X 10 TO ½ INCH 46 1323
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

Figure 50 shows conversion as a function of inlet gas concentration for Runs C9 through C11. In a first order system, the fractional conversion would be independent of concentration. For second order kinetics, conversion would be more dependent upon concentration than our results show. Our system appears to be somewhere in between first and second order.

Table 62 gives the analysis of the aqueous product liquid remaining at the end of the run. The pH, sulfur and sulfate figures are consistent with earlier recycle data. Since the liquid from the later runs was in the column for the entire run, it represents more residence time than the longest recycle run. The absence of change in the liquor composition corroborates the conclusion that no problems will occur due to recycling.

E. Reaction Products - Effect on Rate of Sulfur Production

At first it was thought that conversion was low early in a run due to the time required to build up an inventory of slowly draining sulfur in the column. Washes of the column after Runs C7 and C8, gave 7 to 9 grams of sulfur, respectively. This was not sufficient to account for the sulfur that should have been made during the first two hours if the rate were the same as the average of the last four hours. Thus, the buildup of some component in the liquid which improves conversion is indicated.

Figure 48 shows the rate of sulfur production as a function of time for the recycle runs in which the height of packing was progressively reduced. If the delay in reaching final level of conversion were due to slow drainage of sulfur, one would expect the delay to decrease as the height of packing was reduced. Such was not the case, and it appears that there is simply an initiation period in which compounds that are beneficial to the reaction buildup.

The above conclusion fits the earlier observation that the conversion was higher in recycle Run C6 than in the once-through Run C3.

Table 61 shows that Runs C9 and C10 did not experience a significant initiation period. Presumably this was due to the liquid not being circulated so that beneficial products accumulated rapidly. Run C11 did show an initiation period but this may have been due to sampling difficulties as well as the low concentration of sulfur in the feed gas. Run C5 also did not display an initiation time, and this may have been due to the presence of thiosulfate and its decomposition products in the liquid feed.

Using a batch aqueous Claus system at ambient conditions, Mathieu(20) found it required about 20 minutes for desulfurization to reach 90% of its maximum value, and about 100 minutes to attain the maximum value.

Corrosion

Our reaction medium is potentially very corrosive. The stainless steel valve through which sulfur was drained showed pitting. The column was not examined under magnification, but there was no obvious corrosion or scaling.

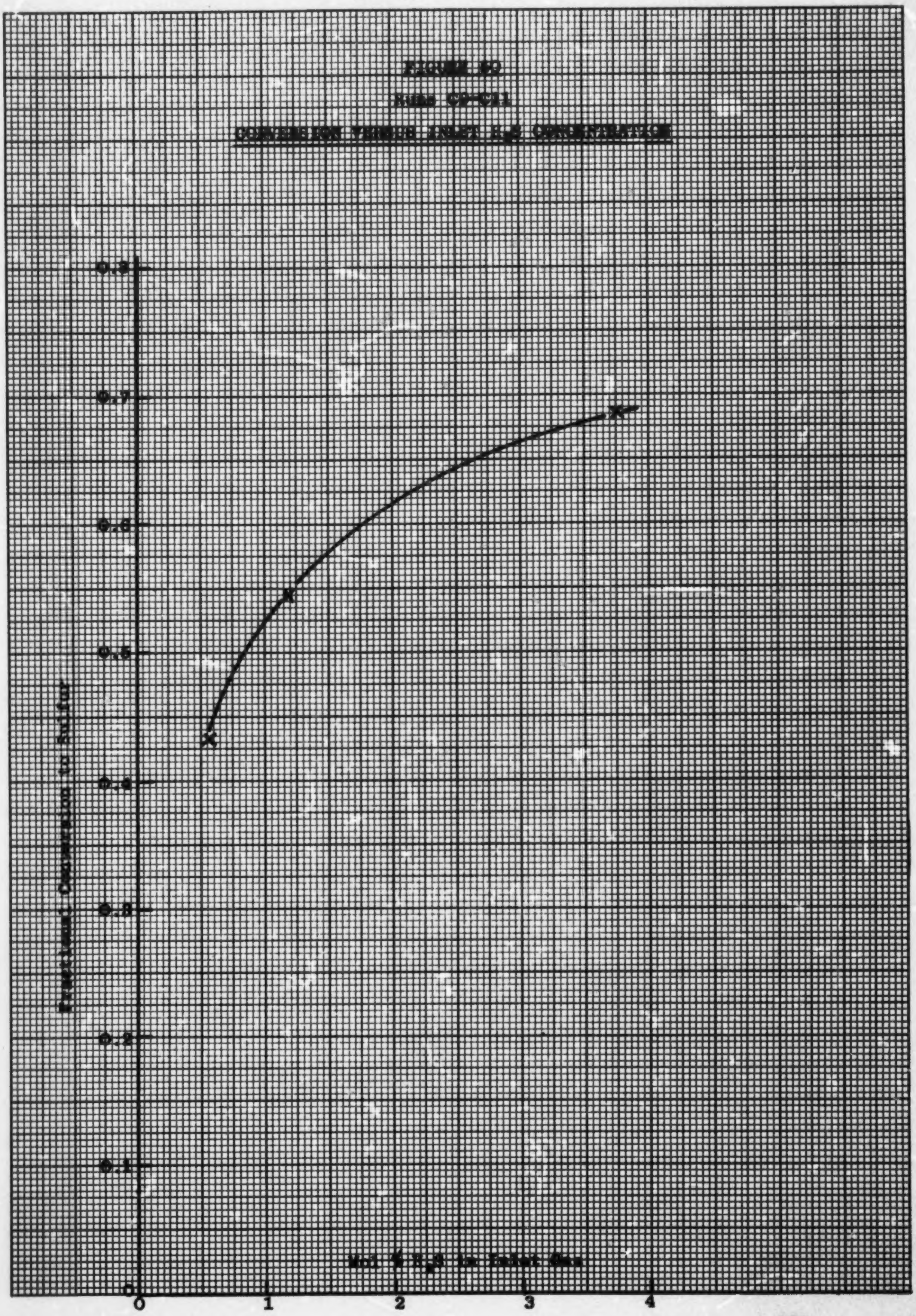


FIGURE 60

Runs CP-C11

CONVERSION VERSUS INLET H_2S CONCENTRATION

K+E 10 X 10 TO ½ INCH 46 1323
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

F. Conclusions

The liquid-phase Claus reaction proceeds readily under simulated process conditions. There is no build up of acidity, sulfur or sulfate as the solvent liquor is exposed to the reaction. Conversions corresponding to over 90% conversion of the feed sulfur have been demonstrated.

The reactor volume needed to reach 90% recovery of sulfur via the liquid-phase Claus is in the range given in the previous process estimate.(1)

The system has a gas concentration dependence between first and second order.

XII. GASIFICATION KINETICS

A. Introduction

Four series of gasification kinetics runs were made to supply information needed for gasifier design. Two temperatures (1620 and 1700°F) and two carbon burnoff levels (nominally 30% and 60%) were used. All runs were made with chars produced from a Pittsburgh Seam coal from the Loveridge Mine.

To avoid large changes in the partial pressures of the reactants and products over the length of the gasifier bed, run conditions were chosen to give low gasification rates.

B. Method

The reactor was the 4 inch I.D. vessel used in the coal pretreatment studies. A flow diagram of the system is given in Figure 13.

The inlet gases were various mixtures of steam, recycle gas, and added N_2, H_2, and CO_2 to give the desired inlet partial pressures. By varying the ratio of added H_2 and CO_2, the desired inlet partial pressure of CO was obtained after the entire inlet gas mixture had reached water gas shift equilibrium. Experience has shown that this equilibrium is established rapidly in the bottom of the reactor.

Char was fed continuously and the unreacted product was removed continuously via an overflow weir which controlled the bed height at 41 inches. The weight of material in the bed was measured by the pressure drop across the entire bed.

The runs in each of the four series were made continuously and sequentially, except for weekend shutdowns. Temperature and inlet gas flows and compositions were held constant for at least three nominal bed inventory changes and then at least two, 2-hour balance periods were made. The inlet gas condition then was changed to that for the next run and the above procedure was repeated. In all, 26 runs were made.

C. Feedstock Preparation

Preparation of the feedstocks for both 30% burnoff series is described in Section V. The feedstocks for the two 60% burnoff series were the composited products, including the lineout material, from the corresponding 30% burnoff series.

D. Data Workup

The data workup was straightforward, being based on measured values for the input and output streams, the dry exit gas rates, condensate rates (unreacted steam), and the dry product gas analyses. The gas chromatograph used for the product gas analyses was not designed to give complete resolution of CO and N_2. The resolution is such that the CO content can be measured to within 10%, e.g., 10 ± 1%, which is sufficient for most purposes. In this study, the CO content of the dry gas was calculated to correspond with water gas shift equilibrium in the total gas leaving the top of the bed.

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E. Results

The compositions of the four feedstocks which were used are given in Table 63. Properties of the char products are shown in Table 64. Run conditions and results for the 1620°F and 1700°F runs are in Tables 65 and 66, respectively.

Some of the entries in the tables are given with more significant figures than the accuracy of the data warrants. This was done only to avoid errors due to rounding.

Results from two runs, K3A and K16A, are not included in the tables. Steady state never was reached in these runs because of char feeder aberrations.

F. Correlation of Rates

For correlative purposes the assumption was made that an "effective" gas composition can be assigned to each run. For this work the effective gas compositions were taken, somewhat arbitrarily, as 90% of the outlet gas partial pressure plus 10% of the inlet gas partial pressures listed in Tables 65 and 66.

Rate correlations were attempted using the reaction models developed in an earlier study with lignite and subbituminous coal chars(3,7,21) but without success.

Table 67 gives the reaction rates, effective partial pressures, and the mean burnoff level for each run.

G. Conclusions

In the absence of any kinetics data for bituminous coal chars which involve the combined inhibiting effects of both H_2 and CO, our process estimates assumed a total gasification rate of 1/15 the rate predicted by our kinetics correlation for lignite char gasification.(3,7)

Comparison of the calculated rates (multiplied by 1/15) for the effective partial pressures given in Table 67 with the rates measured at high levels of inhibition shows that the calculated rates are considerably higher and that the deviation becomes greater as the H_2/CO ratio increases. Although we have no new data at low levels of inhibition at process conditions, the end result undoubtedly will be that the total gasification rate will be lower than previously predicted.

The process implication is that more steam will be needed in the gasifier, which in turn will decrease the thermal efficiency. Design calculations cannot be made until the new data are correlated successfully. Additional experimental data are desirable in order to achieve a more reliable correlation.

Table 63

Feedstock Compositions for Kinetics Study

Feedstock Used in Run	K1 → K7	K1A → K7A	K10 → K16	K10A → K16A
Hydrogen, Wt. % (dry basis)	.66	.53	.52	.41
Carbon	84.32	82.93	84.72	82.20
Nitrogen	1.34	.78	1.32	.71
Oxygen (by difference)	-.77	-.58	-.98	-1.00
Sulfur	2.03	1.12	1.85	1.15
Ash	12.50	15.22	12.63	16.53
Size, Tyler Mesh, Wt. %				
28 x 35	17.7			
35 x 48	30.5			
48 x 65	30.9			
65 x 100	18.9			
-100	2.0			
Particle Density, lb/ft^3				
28 x 35	89.4			
35 x 48	90.5			
48 x 65	89.8			
65 x 100	91.0			
-100	85.2			

Table 64

Properties of Products from Gasification Kinetics Runs

Product from Run	K1	K2	K3	K4	K5	K6	K7	K2A	K4A	K5A	K6A	K7A
Hydrogen, Wt. $ (dry basis)	.54	.57	.59	.58	.62	.59	.53	.53	.54	.51	.55	.53
Carbon	82.56	82.96	81.84	82.81	82.17	83.27	82.86	80.05	78.64	78.25	79.47	79.71
Nitrogen	.72	.73	.75	.73	.70	.77	.89	.61	.64	.61	.62	.60
Oxygen (by difference)	-.44	-.56	-.97	-.61	-.16	-.62	-.34	+.18	-.25	+.05	+.08	-.17
Sulfur	1.27	1.16	1.38	1.04	1.00	1.10	1.40	.44	.35	.35	.38	.62
Ash	15.35	15.14	16.41	15.45	15.67	14.89	14.66	18.19	20.08	20.23	18.90	18.71
Size, Tyler Mesh, Wt. $												
+28	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
28 x 35	12.6	14.0	12.1	17.5	14.3	14.3	17.5	10.9	12.1	15.7	13.9	15.5
35 x 48	33.9	34.2	33.2	32.9	32.5	32.8	31.1	33.6	31.7	33.8	31.3	35.1
48 x 65	32.0	31.4	32.6	30.9	31.9	32.3	29.9	33.1	31.7	30.6	30.7	29.2
65 x 100	19.6	18.4	20.5	17.3	19.2	18.7	18.9	20.3	21.6	17.6	21.3	17.5
-100	1.9	2.0	1.6	1.4	2.1	1.9	2.6	2.1	2.9	2.3	2.8	2.7
Density of Fraction, lb/ft³												
28 x 35	78.2	77.5	78.2	82.0	79.0	86.2	80.8	73.4	74.5	70.4	74.5	73.7
35 x 48	78.0	81.4	76.4	79.8	80.7	82.2	84.2	71.8	71.8	66.8	68.6	73.7
48 x 65	72.9	80.1	70.9	76.9	79.9	81.8	83.0	71.9	67.2	71.2	70.8	73.3
65 x 100	73.1	79.3	75.9	80.6	76.8	81.2	83.4	71.6	70.0	67.4	72.1	69.9
Mean Density, lb/ft³⁽¹⁾	76.8	80.0	74.6	79.4	79.3	82.4	83.0	71.9	70.1	68.8	70.9	72.8
Mean Diameter, inch⁽²⁾	.0119	.0120	.0118	.0124	.0120	.0120	.0122	.0117	.0116	.0122	.0118	.0122

Product from Run	K10	K11	K12	K13	K14	K15	K16	K11A	K12A	K13A	K14A	K15A
Hydrogen, Wt. $ (dry basis)	.36	.40	.39	.40	.43	.41	.42	.41	.32	.32	.34	.42
Carbon	81.81	81.99	80.77	81.07	81.21	82.73	83.00	78.89	75.09	76.18	75.52	77.89
Nitrogen	.66	.65	.67	.68	.67	.67	.71	.52	.53	.52	.50	.49
Oxygen (by difference)	-1.01	-.53	-1.31	-.53	-.66	-1.01	-.89	-1.27	-.11	-.33	-.42	-.90
Sulfur	1.23	1.12	1.31	.89	1.02	1.00	1.27	.49	.51	.31	.34	.30
Ash	16.95	16.37	18.17	17.49	17.33	16.20	15.49	20.96	23.66	23.00	23.72	21.80
Size, Tyler Mesh, Wt. $												
+28	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
28 x 35	14.6	15.8	12.6	15.9	17.9	18.5	11.9	17.2	11.1	12.5	11.4	14.2
35 x 48	33.5	31.8	31.2	34.0	32.2	33.5	33.0	34.0	32.6	33.3	32.2	33.6
48 x 65	30.6	31.4	32.4	31.4	30.5	29.0	36.2	30.1	35.4	31.6	32.9	31.2
65 x 100	18.5	18.3	20.6	16.9	17.1	17.0	18.4	16.3	19.6	20.0	20.6	18.9
-100	2.6	2.7	3.2	1.8	2.3	2.0	1.5	2.4	1.3	3.6	2.9	2.1
Density of Fraction, lb/ft³												
28 x 35	77.2	79.2	76.6	76.8	77.6	80.7	80.7	67.9	67.2	69.0	65.7	69.5
35 x 48	76.3	75.6	72.9	75.1	73.9	79.2	80.6	66.5	63.2	61.6	64.4	64.1
48 x 65	76.6	75.3	73.4	75.5	72.6	77.6	81.1	67.5	58.1	61.0	66.2	62.8
65 x 100	76.6	77.4	72.5	73.9	76.8	79.5	81.0	67.7	62.6	69.4	61.8	62.8
Mean Density, lb/ft³⁽¹⁾	76.6	76.4	73.4	75.3	74.8	79.1	80.9	67.2	61.3	63.9	65.1	64.1
Mean Diameter, inch⁽²⁾	.0120	.0121	.0116	.0123	.0124	.0125	.0118	.0124	.0117	.0117	.0116	.0120

(1) Reciprocal mean.
(2) Arithmetic mean.

Table 65

Conditions and Results for 1620°F Runs
System Pressure: 15 atm (206 psig)
Reactor ID - 4" Bed Height - 41"

Run No.	K1	K2	K3	K4	K5	K6	K7	K2A	K4A	K5A	K6A	K7A
Feedstock	← Loveridge Char Treated at 1600°F →							← Composite K1 - K7 Product →				
Feedrate, lb/hr MF	1.69	2.26	2.89	3.20	3.94	3.96	4.62	1.66	2.10	2.50	2.60	3.05
Recycle Fluidizing Gas, SCFH	97.0	72.9	78.2	19.8	.0	.0	43.1	68.7	21.3	.0	.0	48.6
Recycle Lift Gas, SCFH	70.5	69.9	71.5	65.6	69.2	65.5	68.7	67.3	65.7	68.8	65.6	68.5
Inlet Gas												
Steam, SCFH	65.5	93.5	147.0	153.5	187.2	136.8	138.5	95.6	150.9	176.9	136.3	159.5
H_2	18.0	34.0	.0	46.0	28.0	80.0	.0	34.0	47.0	32.0	78.0	.0
CO_2	18.0	14.0	40.0	32.0	53.0	.0	.0	21.0	32.0	51.0	.0	.0
N_2	61.0	39.0	.0	16.0	.0	49.0	65.0	51.0	8.0	.0	47.0	49.0
Total Inlet Gas, SCFH	330.0	323.3	336.7	332.9	337.4	331.3	315.3	337.6	324.9	328.7	327.2	325.6
Purges (N_2) above Bed, SCFH	← 15.0 →											
Inlet Gas Partial Pressure, atm												
H_2O	3.025	4.348	6.256	6.978	8.181	5.913	6.105	4.360	7.063	8.159	5.970	6.697
H_2	1.803	3.137	1.387	2.899	1.758	4.812	1.315	2.509	3.040	1.934	4.788	1.238
CH_4	.070	.117	.087	.099	.066	.098	.082	.077	.101	.057	.086	.065
CO	.985	.879	1.181	.891	.780	.113	.174	.883	.955	.863	.094	.143
CO_2	1.309	.965	4.220	1.698	2.877	.110	.638	1.215	1.757	2.883	.093	.612
N_2	7.809	5.554	1.870	2.435	1.337	3.953	6.685	5.958	2.086	1.104	3.969	6.245
Outlet Gas												
Product Gas, SCFH	146.7	137.4	111.9	154.6	167.0	189.2	158.3	149.6	137.1	141.5	178.4	144.2
N_2 Purges	← 15.0 →											
Condensate	56.8	82.8	121.4	133.9	161.3	116.7	97.0	88.5	137.2	160.8	118.3	131.0
Total Outlet Gas, SCFH	356.0	348.0	368.0	358.9	382.5	356.4	352.1	359.1	346.3	356.1	347.2	377.3
Fluidizing Velocity, at top of Bed, ft/sec	.306	.299	.316	.308	.328	.306	.302	.308	.297	.306	.298	.324
Partial Pressures, at top of Bed, atm												
H_2O	2.390	3.564	4.947	5.598	6.326	4.906	4.133	3.700	5.946	6.771	5.113	5.205
H_2	2.176	3.490	2.111	3.475	2.718	5.040	2.567	2.800	3.465	2.619	4.972	2.300
CH_4	.126	.223	.143	.270	.210	.372	.185	.158	.254	.168	.317	.134
CO	1.467	1.288	2.113	1.449	1.583	.476	.809	1.215	1.393	1.439	.378	.560
CO_2	1.278	1.042	3.925	1.847	2.820	.367	1.032	1.270	1.892	2.948	.308	1.004
N_2	7.563	5.392	1.761	2.361	1.343	3.839	6.274	5.858	2.048	1.056	3.912	5.797
Product Gas Composition, mol %												
H_2	16.48	28.93	19.81	34.64	29.36	47.04	22.30	23.44	35.67	29.58	47.13	22.17
CH_4	.95	1.85	1.34	2.69	2.27	3.47	1.61	1.32	2.63	1.89	3.00	1.39
CO	11.09	10.67	19.83	14.44	17.09	4.44	7.02	10.17	14.25	16.29	3.56	5.40
CO_2	9.66	8.64	36.83	18.41	31.53	3.42	8.97	10.63	19.48	33.29	2.93	9.66
N_2	61.86	49.90	22.19	29.83	19.76	41.63	60.10	54.44	27.98	18.99	43.38	61.46
% Steam Conversion	18.4	15.5	16.0	17.3	16.8	14.6	27.9	13.7	14.3	12.2	13.1	16.3
Char Bed Density, lb/ft³	31	33	31	32	32	31	34	29	30	29	29	29

Table 66

Conditions and Results for 1700°F Runs
System Pressure: 15 atm (206 psig)
Reactor ID - 4" Bed Height - 41"

Run No.	K10	K11	K12	K13	K14	K15	K16	K11A	K12A	K13A	K14A	K15A
Feedstock	← Loveridge Char Treated at 1700°F →							← Composite K10 - K16 Product →				
Feedrate, lb/hr MF	1.78	2.24	2.80	3.18	3.86	3.91	4.60	1.49	1.89	2.06	2.44	2.60
Recycle Fluidizing Gas, SCFH	117.8	95.2	119.7	60.2	47.8	35.3	87.7	95.3	118.1	59.2	47.5	35.3
Recycle Lift Gas, SCFH	70.4	68.8	71.1	67.9	70.1	66.8	70.1	68.9	70.1	66.8	69.6	66.9
Inlet Gas												
Steam, SCFH	52.3	68.7	118.3	122.1	139.2	108.6	115.8	69.5	111.1	118.5	141.7	102.2
H_2	18.0	34.0	.0	50.0	32.0	83.0	.0	36.0	.0	51.0	32.0	85.0
CO_2	23.0	19.0	46.0	29.0	53.0	.0	.0	19.0	45.0	32.0	52.0	.0
N_2	64.0	46.0	.0	11.0	.0	45.0	55.0	44.0	.0	11.0	.0	47.0
Total Inlet Gas, SCFH	345.5	331.7	355.1	340.2	342.1	338.7	328.6	332.7	344.3	338.5	342.8	336.4
Purges (N_2) above Bed, SCFH	← 15 →											
Inlet Gas Partial Pressure, atm												
H_2O	2.411	3.268	4.739	5.569	6.296	4.574	4.752	3.334	4.592	5.531	6.461	4.426
H_2	1.751	2.997	1.433	3.747	2.374	5.688	2.056	3.061	1.274	3.584	2.350	5.749
CH_4	.056	.097	.101	.130	.093	.123	.077	.095	.091	.122	.085	.116
CO	1.497	1.401	2.027	1.496	1.692	.274	.515	1.363	1.933	1.538	1.656	.211
CO_2	1.438	1.065	4.676	1.550	3.129	.154	.829	1.035	4.860	1.654	3.174	.113
N_2	7.847	6.172	2.024	2.508	1.416	4.188	6.771	6.113	2.249	2.571	1.273	4.384
Outlet Gas												
Product Gas, SCFH	161.0	152.9	120.2	159.6	161.2	197.8	157.3	146.6	111.8	149.1	148.0	189.3
N_2 Purges	← 15 →											
Condensate	44.7	56.8	92.2	106.9	118.3	83.5	73.8	62.4	89.9	109.8	124.9	84.0
Total Outlet Gas, SCFH	378.9	358.7	388.2	379.6	382.4	368.4	373.9	358.2	374.9	369.9	375.0	360.5
Fluidizing Velocity, at top of Bed, ft/sec	.338	.320	.346	.338	.341	.328	.333	.319	.335	.330	.334	.321
Partial Pressures, at top of Bed, atm												
H_2O	1.767	2.375	3.563	4.230	4.641	3.401	2.959	2.613	3.588	4.451	4.999	3.495
H_2	2.181	3.404	2.005	4.313	3.161	6.022	3.216	3.386	1.773	4.011	3.039	5.964
CH_4	.099	.181	.155	.274	.205	.348	.142	.174	.137	.255	.182	.326
CO	2.230	2.065	3.296	2.277	2.807	.866	1.501	1.883	3.060	2.158	2.599	.646
CO_2	1.261	1.006	4.079	1.556	2.871	.341	.964	1.014	4.315	1.668	2.983	.264
N_2	7.462	5.968	1.903	2.350	1.316	4.021	6.218	5.930	2.127	2.457	1.198	4.306
Product Gas Composition, mol%												
H_2	15.78	25.68	16.70	37.87	28.87	49.31	25.45	26.03	14.81	35.96	28.65	49.19
CH_4	.72	1.37	1.29	2.41	1.87	2.85	1.12	1.33	1.15	2.29	1.72	2.69
CO	16.14	15.58	27.45	20.00	25.63	7.09	11.88	14.47	25.55	19.35	24.48	5.33
CO_2	9.13	7.58	33.97	13.66	26.22	2.79	7.63	7.80	36.03	14.95	28.11	2.18
N_2	58.23	49.80	20.59	26.06	17.41	37.95	53.92	50.36	22.46	27.45	17.04	40.61
% Steam Conversion	22.9	24.8	20.0	19.0	20.7	22.6	32.2	19.2	17.4	15.8	17.81	19.6
Char Bed Density, lb/ft³	31	30	30	32	29	30	34	29	30	27	28	25

Table 67

Kinetics Summary
System Pressure 15 atm

Run No.	K1	K2	K3	K4	K5	K6	K7	K2A	K4A	K5A	K6A	K7A
Temperature, °F	←1620→											
Feedstock	←Loveridge Char Treated at 1600°F→							←Composite K1 - K7 Product→				
Mean Burnoff, %	30	25	32	26	30	20	22	44	48	49	42	46
15 - P_{N_2}	6.13	8.56	9.27	10.80	10.83	10.81	7.69	7.87	11.07	11.00	10.80	8.16
Effective Partial Pressure, atm												
H_2O	2.454	3.642	5.078	5.736	6.512	5.007	4.330	3.766	6.058	6.910	5.199	5.354
H_2	2.139	3.455	2.039	3.417	2.622	5.017	2.442	2.771	3.423	2.551	4.954	2.194
CO	1.419	1.247	2.020	1.393	1.503	.440	.746	1.182	1.349	1.381	.350	.518
CH_4	.120	.212	.137	.253	.196	.345	.175	.150	.239	.157	.294	.127
Gasification Rate*												
Total Gasification Rate, measured	9.60	9.74	17.68	15.39	21.48	14.88	17.72	9.31	14.50	17.46	12.86	18.14
Methane Formation Rate, "	.97	1.64	1.06	2.78	2.54	4.54	1.62	1.50	2.89	2.14	4.06	1.38
Total Gasification Rate, "calculated"	28.0	41.5	35.6	55.4	60.4	100.8	86.2	48.3	60.0	70.0	115.8	136.3

Run No.	K10	K11	K12	K13	K14	K15	K16	K11A	K12A	K13A	K14A	K15A
Temperature, °F	←1700→											
Feedstock	←Loveridge Char Treated at 1700°F→							←Composite K10 - K16 Product→				
Mean Burnoff, %	39	30	38	33	32	24	26	57	65	59	60	49
15 - P_{N_2}	6.22	8.00	8.95	11.06	10.78	10.64	7.78	8.04	8.49	10.86	10.79	10.44
Effective Partial Pressure, atm												
H_2O	1.831	2.464	3.681	4.364	4.807	3.518	3.138	2.685	3.688	4.559	5.145	3.588
H_2	2.138	3.363	1.948	4.256	3.082	5.989	3.100	3.354	1.723	3.968	2.970	5.943
CO	2.157	1.999	3.169	2.199	2.696	.807	1.402	1.031	2.947	2.096	2.506	.603
CH_4	.095	.173	.150	.260	.194	.326	.136	.16[illegible]	.132	.242	.172	.306
Gasification Rate*												
Total Gasification Rate, measured	13.46	13.34	21.38	19.88	25.24	18.29	20.67	12.30	30.11	19.50	23.68	17.42
Methane Formation Rate, "	.82	1.50	1.13	2.67	2.27	4.09	1.13	1.54	1.02	2.94	2.11	4.59
Total Gasification Rate, "calculated"	33.4	46.1	34.7	63.6	53.6	148.2	91.0	56.2	38.3	70.8	63.0	167.8

*Units are: lb carbon gasified/minute/lb carbon in bed x10^4

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Appendix A

Detailed Investment Costs

Table A-1

Cost Estimate: Section 300; Sulfur Removal

	Equipment	Number	Description	Weight #	Material $	Labor $	Insulation □'	Electrical H.P.	Structural #	Foundations C.Y.	Piling 50 T Ea.
Major	Steam Super Heaters	C-301	6 Ea. 1535□' 1-1 Pass. Float Hd., 1650°F, 230#, 316 S.S. Tube	160,800	198,600	7,200	3,780		75,900		
	Waste Heat Boiler	C-302	8 Ea. 2120□' 1-1 Pass. Float Hd., 1600°F, 230#, 2-1/4 Cr-1Mo Tube	280,000	228,000	12,000	6,240		67,900	30	30
	Intercoolers	C-303	3 Ea. 630 □' U-Tube 28"⌀ Flg. in D-302 75#, 130°F, 304 S.S. Tube	15,000	30,750	750					
	Quench Water Cooler	C-304	3400 □', 1-1 Pass. Fix. Hd., 125# 304 S.S. Tube	67,000	43,000	1,200			1,000	3	
	Trim Cooler	C-305	175 □', U-Tube, C.S., 30"⌀ Shell x 10'L, 3/4"⌀ Tube x 14 B.W.G.	3,000	2,400	150			400	1	
	Quench Water Cooler	C-304	3400 □', 1-1 Pass. Fix. Hd., 125# 304 S.S. Tube	22,000	42,000	1,200			1,000	3	
	Sulfur Reactor	D-301	6 Ea., 21'-6"O.D. x 47'O.S.S., 230#, 1700°F, Refr. Lined, C-St	4,705,800	1,064,400	1,020,600	28,800			238	110
	Regen. Reactor	D-302	2 Ea. 21'-3"O.D. x 58'O.S.S., 230#, 1300°F, Refr. Lined, C-St	1,802,000	407,400	394,300	11,000			139	48
	Acceptor Converter	D-303	3 Ea. 5' I.D. x 7'-6"O.S.S., 15#, 130°F, Cone Bot., F&D, 304 S.S.	8,000	11,100	600			1,500		
	Acceptor Feed Hopper	F-300*	10'x10'x45°Cone, 1/4"C.S. ℄ W/Grating, Conc. Base	5,800	1,620	1,480				27	
	Acceptor Surge Bin	F-301	2 Ea. 7'O.D.x10'O.S.S. W/Cone Btm, F&D Top, 1/4" C.S. ℄	8,780	3,960	440					
	Acceptor Lock Hopper	F-302	4 Ea. 8' I.D.x10'O.S.S. W/Cone Btm, Ellip. Top, 5/8" C.S., 250#	40,320	28,000	2,800			4,800		
	Spent Acceptor Lock Hopper	F-303	2 Ea. 7' I.D.x10'O.S.S, Ellip. Hds, 3/4" C.S. ℄ 250#, 1350°F	83,300	23,300	6,300			6,000		
	Quench Water Surge Tank	F-304	8' O.D.x12'O S.S., 15# Des, 3/16"-304 S.S. ℄, Cone Btm.	4,860	5,960	440				3	
	Dust Collectors	G-301	18 Ea. 31,100 ACFM, C. Stl. ℄, 1700°F, 5" Refr. Lining	384,000	289,800	79,300	9,540		36,000		
	Dust Collectors	G-302	18 Ea. 31,100 ACFM, C-St W/5" Refr. Lin., 250#, 1700°F	379,600	275,400	73,000	9,540		36,000		
	Dust Collectors	G-303	4 Ea. 14,000 ACFM, C.S. ℄, 1350°F, 5" Refr. Lining	121,300	57,200	16,000	1,900		12,000		
	Dust Collectors	G-304	4 Ea. 14,000 ACFM, C-St W/5" Refr. Lin., 250#, 1350°F	112,000	54,000	14,800	1,800		11,300		
	Hydroclones	G-305	273 GPM, 4 Ea. 8" Dia., Rubber Lin. Caged W/Piping	4,000	6,100	500			1,000		
	Slurry Pump	J-301	2 Ea. 68 GPM, 32 psi, Aust. I. Centrif. at 1750 RPM	2,100	5,500	200		10		2	
	Black Water Pump	J-302	2 Ea. 1124 GPM, 56 psi, Aust. CDL-5"B at 1180 RPM	5,000	8,020	300		130		7	
	Quench Water Circ. Pump	J-303	2 Ea. 358 GPM, 106 psi, Aust. Iron Centrif. at 1750 RPM	3,600	8,100	400		80		3	
	Make-up CO_2 Comp'r	JC-301	7620 ACFM, 15→240 psia, 2 Stg. W/precooler and Intercool	80,000	193,000	10,000		1,500		33	6
	Acid Gas Comp'r	JC-302	860 ACFM, 15→215 psia, 2 Stg. W/Intercooler, Recip.	34,000	39,300	3,000		300		18	
	CO_2 Blower	JC-303	1430 ACFM, 5 psi, Rotary w/W.C. Bearings, 3600 RPM	3,800	5,600	200		40		3	
	Acceptor Screw Feeder	L-300*	2 Ea. 300 CFM, 35'lg x8" Dia. at 30° Slope Z-H C.S.	3,100	3,420	700		8	400	2	
	Acceptor Elevator	L-301	2 Ea. 300 CFM, 65'C-C, Webster #C-1229 12 BWG Casing	15,820	14,300	3,100		10	11,740	3	
	Acceptor Feeder	L-302	4 Ea. 150 CFM, 6"⌀ Rot. Vane, 100°F, 250#, C.S	9,600	22,000	1,000		8	2,400		
	H Temp. Rotary Feeder	L-303	6 Ea. 2280 CFM, 16"⌀ Rot. Vane, 30"⌀ Flg. Refr. Lin. 250#, 1700°F	42,000	75,000	5,700	300	30	7,300		
	H Temp. Rotary Feeder	L-304	6 Ea. 63 CFM, 6"⌀ Rot. Vane, 18"⌀ Flg., Refr. Lin. 250#, 1700°F	37,000	43,200	4,300	180	12	4,800		
	H Temp. Rotary Feeder	L-305	2 Ea. 205 CFM, 8"⌀ Rot. Vane, 30"⌀ Flg., Refr. Lin. 250#, 1350°F	10,300	16,300	1,600	70	8	1,800		
	Converter Agitator	L-306	2 Ea. 24"⌀ Impeller, 15#, 130°F, 304 S.S.	3,300	8,700	420		15	1,200		
			Totals Major Equipment		3,173,320	1,663,680	73,150	3,137	363,340	484	192
Minor	Piling		M + L at 300		147,000	-					490
	Foundations		M = 60, L = 60		66,000	66,000				1,100	
	Structural		M = .28, L = .22		403,000	317,000			1,440,000		
	Electrical		M = 60, L = 50		206,000	172,000		3,440			
	Insulation		M = .80, L = 1.70		192,000	408,000	240,000				
	Buildings		M = .80, L = .80 at 46,000 CF		37,000	37,000					
	Piping		M_p = .30 Maj. M. L = .70 M_p		951,000	666,000					
	Instrumentation		M_I = .06 Maj. M, L = .40 M_I		190,000	76,000					
			Totals Minor Equipment		2,182,000	1,732,000					
			Total M + L		8,760,000						
	Markup, Incl. Eng., Supervision, Purch., Field, Home Office, Profit and Contingency				6,240,000						
			Total Investment		15,000,000						

*Not shown on Figure 4.

Table A-2

Cost Estimate: Section 400; Sulfur Recovery

	Equipment	Number	Description	Weight #	Material $	Labor $	Insulation $	Electrical H. P.	Structural #	Found's C. Y	Piling 50 T Ea.
Major	Sulfur Combustor	B-401	14"Ø x 34' Lg., 250 psig, Refr. Lined, Water Wall, 88 MM Btu/hr	353,000	83,800	61,800	500		7,800	20	12
	Claus Gas Reheater	C-401A	4 Ea. 5400 Φ, 1"Ø x 16 BWG., 316 S.S. Tube, 22' Lg., 250#, 1300°F, Refr. Lin.	200,000	368,800	12,000	3,270		32,560		
	Claus Gas Reheater	C-401B	4 Ea. 5400 Φ, 1"Ø x 16 BWG., 1Cr—$\frac{1}{2}$ Mo Tube, 22' Lg., 250#, 950°F, C-Mo. Shell	160,000	192,400	8,000	2,940		34,240	17	14
	Heat Exchanger	C-402	4 Ea. 5000 Φ, 1"Ø x 14 BWG., C.S., 20' Lg., 250#, 750°F, C.S. Shell	148,000	140,000	8,000	1,360		2,000	15	
	Tempering Gas Cooler	C-403	1 Ea. 630 Φ, 3/4"Ø x 14 BWG., C.S.,10' Lg., "U" Bend, 250#, 450°F, C.S. Shell	5,000	4,200	300	160		300	2	
	Acid Cooler	C-404	4 Ea. 2800 Φ, 316 S.S. Tubes, 3/4"Øx 16 BWG. "U", 28"Ø C.S. Shell, 250#	72,000	121,200	4,000			4,080	8	
	Recycle Cooler	C-405	4 Ea. 7835 Φ, C.S. Tubes, 3/4"Ø x 14 BWG. Fix. Hd., 1-2 Pass, 250#	240,000	138,000	12,000			7,900	13	8
	Sidestream Coolers	C-406	2 Ea. 3275 Φ, 316 S.S. Tubes, 3/4"Ø x 16 BWG "U", 24' Lg. 1-4 Pass, 250#	40,000	70,800	2,000			600	8	
	Liquid Phase Claus Rx.	D-401	2 Ea. 9'Ø x 90'O.S.S w/skirt, 316 S.S. Clad, 250#, 450°F, Ellip. Hd.	269,000	268,000	22,200	5,800			75	30
	SO_2 Absorber Columns	D-402	2 Ea. 7'3"Ø x 57'O.S.S.w/skirt, 316 S.S. Clad, 250#, 450°F, 44' Pack.	308,780	207,740	18,440				43	12
	Dust Hoppers	F-401	2 Ea. 5'Ø x 10'O.S.S., 250#, 400°F, C.S. Ł w/valves	13,600	10,500	900			5,300		
	Separators	F-402	2 Ea. 14'6"Ø x 16'6" O.S.S., Horiz, 316 S.S. Clad, 250#, 450°F	170,600	120,200	102,400	2,740		6,000	20	8
	Liquid Sulfur Storage Tank	F-403	5'Ø x 15' O.S.S., Horiz, w/Stm. Coil, 14#, 310°F, C.S. Ł	5,320	2,190	560	320			3	
	Recycle Gas Comp'r.	JC-401	3 Ea. 13,200 ACFM, 310°F, 200 → 242 psia, Centrif., 8000 RPM	276,000	630,000	30,000		9,000		106	24
	Centrifugal Air Comp'r.	JC-402	20,900 CFM, 14.7 → 219.7 psia, 2 Stg. w/Intercool, 8000 RPM	180,000	411,000	20,000		7,000		56	12
	Sulfur Pumps	J-401	2 Ea. 25 GPM, 215 psi Rot. Gear, 316 S.S., W.C. Bearings	800	2,540	200	40	15		2	
	Acid Circ. Pumps	J-402	3 Ea. 750 GPM, 210 → 262 psia, Aust. I. Centrif. 1750 RPM	4,200	12,630	450		120		6	
	Acid Sidestream Pumps	J-403	3 Ea. 750 GPM, 210 → 216 psia, Aust. I, Centrif, 1150 RPM	3,000	9,060	450		30		6	
	B.F. Water Pumps	J-404*	2 Ea. 1232 GPM, 0 → 250 psig, C.S., 2 Stg. Centrif, 1750 RPM	8,600	13,400	600		500		14	
	Absorber R. C. Pumps	J-405	3 Ea. 750 GPM, 200 → 310 psia, C.S., Centrif. 1750 RPM	8,400	14,070	450		300		10	
	Elec.-Static Precipitator	L-401	2 Ea. 14,400 ACFM, 380 °F, 210 psia, 1 Stg. 86-8"Ø Tubes	200,000	236,000	20,000		80	27,940	17	
			Totals Major Equipment		3,056,530	324,750	17,130	17,045	128,720	441	120
Minor	Piling		M + L = 300		63,000	-					210
	Foundations		M = 60, L = 60		42,000	42,000				700	
	Structural		M = .28, L = .22		115,000	90,000			410,000		
	Electrical		M = 60, L = 45		1,033,000	774,000		17,220			
	Insulation		M = .80, L = 1.70		24,000	51,000	30,000				
	Buildings		M = .60, L = .60 at 100,000 C.F.		60,000	60,000					
	Piping		M_p = .25 Maj. M., L = .60 M_p		764,000	458,000					
	Instrumentation		M_I = .06 Maj. M., L = .40 M_I		92,000	37,000					
			Totals Minor Equipment		2,193,000	1,512,000					
			Total M + L =		7,086,280						
	Mark-up, Including Eng'r., Purchasing, Superv., Field, Home Office, Profit & Conting.				4,313,720						
			Total Investment		$11,400,000						

*Not shown on Figure 4.

Table A-3

Cost Estimates: Section 600; Wet Gas Scrubbing and Reheat

	Equipment	Number	Description	Weight #	Material $	Labor $	Insulation □'	Electrical H. P	Structural #	Foundations, C. Y.	Piling 50 T Ea.
Major	Heat Exchanger	C-601A	8 Ea. 12750 □',250#,1300°F, 316 S.S. Tube 1-1/4"Ø, Cr-Mo Shell	800,000	1,408,000	40,000	13,720		17,650		
	Heat Exchanger	C-601B	8 Ea. 12750 □', 250#,1100°F, Cr-Mo Tube, 1-1/4"Ø,C.S. Shell	920,000	796,000	48,000	9,160		23,200		
	Heat Exchanger	C-601C	8 Ea. 12750 □', 250#,800°F, C-Si Tube, 1-1/4"Ø,C.S. Shell	920,000	568,000	48,000	6,860		26,450	138	64
	Circ. Water Coolers	C-602	4 Ea. 14350 □', 250#,220°F, C. S. Tube & Shell, 3/4"Ø Tube, Fix. Hd.	480,000	255,600	24,000				26	
	Make-up Water Pumps	J-401	3 Ea. 700 GPM, 243 psi, 2 Stg. Centrif., 3500 RPM, C.S.	13,200	16,740	900		450		18	
	Black Water Circ. Pumps	J-402	3 Ea. 3180 GPM, 58 psi, 1 stg. Centrif, 1750 RPM, Cr-Stl.	20,100	23,190	1,800		600		45	
	Surge Drums	F-601	2 Ea. 10,000 Gal. 9'Ø x 21' O.S.S., Vert. C.S., 250#, Ellip. Hd.	104,120	43,800	5,200			3,300	48	
	Venturi Scrubbers	L-601	4 Ea. 39750 CFM at 500°F, 250#, C.S. Drum w/Cr-Stl. Ajd. Throat	188,000	142,400	13,200	4,180	—	47,230	—	—
			Total Major Equipment		3,253,730	181,100	33,920	1,050	117,830	275	64
Minor	Piling		M + L = 300		21,000	-					70
	Foundations		M = 60, L = 60		22,800	22,800				380	
	Structural		M = .28, L = .22		50,400	39,600			180,000		
	Electrical		M = 60, L = 55		69,000	63,000		1,150			
	Insulation		M = .80, L = 1.70		72,000	153,000	90,000				
	Buildings		M = .60, L = .60 x 10,000 C.F.		6,000	6,000					
	Piping		M_P= .15 Maj. M, L = .60 M_P		488,000	293,000					
	Instrumentation		M_I= .02 Maj. M, L = .40 M_I		65,000	26,000					
			Total Minor Equipment		794,200	,400					
			Total M + L =		4,832,430						
	Mark-up, including Eng'r., Superv., Purchasing, Field, Home Office, Profit & Cont'g.				1,767,570						
			Total Investment		$6,600,000						

APPENDIX B

Literature Survey of Liquid-Phase Claus Reaction

Introduction

The product of the reaction of H_2S with SO_2 in water is called Wackenroder's solution. Therefore, "Wackenroder Reactor" was chosen as a convenient title for characterizing the process sulfur recovery scheme. However, the reaction,

$$2\ H_2S + SO_2 \xrightarrow{\text{(solvent)}} 2\ H_2O + 3\ S,$$

also is equivalent to the Claus reaction which is more widely recognized. In this study, the above reaction will be called the liquid-phase Claus reaction in order to include non-aqueous solvents

Literature references in this section refer to the list on pages 215 and 216.

Aqueous Solvents

When H_2S and SO_2 react in an aqueous medium, byproducts such as thiosulfate and polythionic acids ($H_2S_xO_6$) may occur. Schroeter(1) reviews the relevant reactions in some detail. Side reactions may be minimized by maintaining the ratio H_2S/SO_2 at 2.0.

Dupasquier(2) reported that production of polythionates increases with temperature in the range of 0-25°C. On the other hand, Mathieu(3) reports that polythionic acid formation is minimal at about 50°C, and sulfur recovery is at a maximum. No literature data for high temperatures (150°C, 300°F) have been found.

In 1933, Lincoln(4) patented a process in which H_2S was contacted with sulfurous acid to produce sulfur. He claimed that a slight excess of SO_2 was desirable to insure complete removal of H_2S.

Rosenstein(5) proposed use of only a catalytic amount of liquid water on a packing of insoluble aluminum compounds. The reaction was to be carried out above the melting point of sulfur.

Continental Oil Company(6) patented the use of up to 5% of an aliphatic alcohol in water as the reaction medium.

Leahy(7) suggested the use of at least two electrolytes with unlike ions as additives. Townend and Kelly(8) proposed the addition of 0.5 to 5% aluminum sulfate plus 1 to 5% sulfuric acid.

In a patent granted to SNPA,(3) the use of an aqueous solution containing 10 to 20 grams sodium chloride and 0.6 to 85 grams magnesium sulfate per liter is disclosed. Sea water is included as a solvent. It is claimed that sulfur removal remains high as the liquid is cycled.

Modell, et al.(9) investigated use of the liquid-phase Claus reaction for possible use in stack gas clean-up operations. They used water at 30°C and SO_2 concentrations of 200-7000 ppm. At this writing, results are incomplete.

The Bureau of Mines(10) has disclosed work on a process, which makes use of the liquid-phase Claus reaction, to clean up SO_2-bearing stack gases. Sulfur dioxide is first absorbed in a citrate buffer solution. It is then reacted with a stoichiometric volume of H_2S in a stirred vessel at 50-70°C. It is claimed that the reaction can be brought to completion in one minute. Stauffer's Aquaclaus Process(11) is similar to the USBM process, but the buffer material in the Stauffer process has not been disclosed.

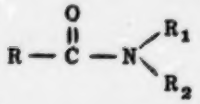
Water Plus Organic Solvents

Townsend(12,13) teaches the use of an organic solvent containing dissolved water. The solvent is to contain at least two non-CH atoms, at least one lower chalcogen such as oxygen or sulfur, and no more than two vicinyl hydroxy radicals. The patent lists over 40 specific solvents, but glycols are preferred. Water is claimed to be catalytic for the reaction, but harmful in large concentrations.

Stolfa, et al.(14) claim the use of water-saturated hydrocarbons together with a catalytic amount of free water. Various aromatic compounds, straight chain paraffins, cyclic paraffins, and olefinic hydrocarbons are listed. A similar patent(15) discloses the use of a detergent additive to improve the recoverability of the sulfur product from the above solvents.

Shell Oil(16) patented a process which conducts the reaction in a medium consisting of 70-98% organic sulfone, 2-20% water, 0.1-10% ferrous salt, and a chelating agent.

Urban and Massey(17,18,19) teach the use of from 0.5 to 40% by volume of water in any alcohol, any ester, or any carboxamide having the general formula,



Water-Free Solvents

In 1909 Feld and Jahl(20) patented the use of tar oils as a solvent for conducting the Claus reaction. They indicated that basic organic nitrogen compounds in the tar were beneficial to the reaction.

A German patent(21) in 1941 referred to the use of an alkylated aromatic base such as dimethylaniline.

Renault(22) patented the use of liquid esters of phosphoric acid. A variation of the process was to add an alkaline agent such as soda, potash, alkali metal sulfides, an amine, or an ammonia type compound.

Eickmeyer(23) suggested use of liquid sulfur as an absorption and reaction medium for the Claus reaction.

Freeport Sulfur Company(24) patented a process using liquid sulfur as the solvent with a base nitrogen compound as a catalyst. A major advantage of this process is that the reaction product is the same as the reaction medium, and therefore no separation step is required.

I.F.P. (Institut Francais du Petrole)[25] teaches the use of a solvent containing an alkali or alkaline earth salt of an organic monocarboxylic acid, polycarboxylic acid or partial esters of them. Polyethylene glycol is the preferred solvent, but numerous others are listed. The process has been commercialized in Japan(26) and Canada.(27)

Summary and Conclusions

The literature shows that a large variety of solvents may be used for the liquid-phase Claus reaction. From the point of view of cost and simplicity, water is by far the best choice.

Any non-aqueous solvent would have to have a low vapor pressure at 320°F in order to limit solvent losses. Ideally the solvent should have a high solubility for H_2S and SO_2 and low solubility for H_2O and S.

Clearly, experimental work is needed to set a design basis for the sulfur recovery section. A priori, water is the best solvent, but non-aqueous systems should not be ignored.

Most of the available literature is in the form of patents. There appears to be little or no reliable data on process yields or kinetics under our proposed operating conditions.

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APPENDIX C

Thermodynamic Data

Introduction

Presented here is a body of self-consistent thermodynamic data for use in equilibrium and heat balance calculations. Some of the data given here were published previously in our 1971 Annual Report to EPA.(1) These data are included here for convenience to the reader.

Previous operations of the continuous unit have shown, that equilibria in many of the possible reactions are approached closely. Apparently, the reasons for this are the high temperatures involved and catalysis by the acceptor and char ash.

Thus, because of close approach, equilibrium calculations provide not only a good check for operation of the continuous unit, but also a reliable guide to predict performance of an actual plant.

Sources of Data

A. Gaseous Phase

Nearly all of the standard free energy of formation values, heat capacities of zero pressure, and the standard heats of formation were taken from the JANAF Thermochemical Tables.(22) The equilibrium constants were calculated from the free energy values, so the set of equilibrium constants is linked and meshed together to give a high degree of consistency. Exceptions in the sources of data were:

1. The heat capacity and heat of formation for $S_{6(g)}$ were calculated from the JANAF tables for $S_{8(g)}$ and the experimental data in the equilibrium constants measured experimentally by Preuner and Schupp.(23)

2. The vapor pressure and heat of vaporization of liquid sulfur were taken from West.(24)

3. The heat content of steam above liquid water were values given in the Keenan and Keyes steam tables.

B. Solid Phase

Sources of data involving calcium compounds are primarily experimental equilibrium measurements which were supported privately by Consol during the 1960's. Consol(25) published equilibrium constant data in the reactions:

$$3/4\ CaSO_4 + 1/4\ CaS = CaO + SO_2 \qquad (1)$$

$$CaO + H_2S = CaS + H_2O \qquad (2)$$

and

$$CaCO_3 = CaO + CO_2 \qquad (3)$$

The results were in agreement and extended the prior experimental measurements of the above reactions.(26,27,28,29)

The reaction,

$$CaCO_3 + H_2S = CaS + CO_2 + H_2O \qquad (4)$$

by which gas desulfurizing and acceptor regeneration occurs is the sum of reactions (2) and (3) above.

For reactions involving solids, we prefer to use experimentally determined values of the equilibrium constants in order to avoid the errors involved in: 1) the use of the sometimes uncertain or discordant free energy values in the literature, and 2) the extrapolation of free energy data to temperatures of interest to the process.

Equilibria in many reactions for which we have no experimental data can be calculated accurately by summing one or more of the reactions (1), (2), and (3) above, with gaseous reactions for which the free energies are well-established. For example, consider the reaction,

$$CaO + 3/4\ S_2 = CaS + 1/2\ SO_2$$

This reaction can be expressed as the sum of the following reactions:

	Equilibrium Constant
$CaO + H_2S = CaS + H_2O$	K12
$H_2O + 1/4\ S_2 = H_2 + 1/2\ SO_2$	$(1K_3)^{1/2}$
$H_2 + 1/2\ S_2 = H_2S$	K2
$CaO + 3/4\ S_2 = CaS + 1/2\ SO_2$	K13

Thus,

$$K13 = \frac{(K12)(K2)}{(K3)^{1/2}}$$

The above equilibrium constants are those identified in Tables C-2 and C-7.

Presentation of Data

Distribution of sulfur vapor species are presented in Table C-1.

Equilibrium constants for gas reactions are shown in Table C-2 and numerical values of the constants as a function of temperature are in Table C-3. Heat capacities are in Table C-4 and the mean heat capacities above 60°F, derived from the Table C-4 data, are in Table C-5. The heat content of steam above liquid water at 60°F also is given in Table C-5.

Heats of formation and heats of reaction at 25°F are given in Table C-6. Equations for the vapor pressure of liquid sulfur are shown in Figure C-1, which is a plot of the equations. An equation for the heat of vaporization of liquid sulfur also is given in Table C-6.

Equilibria for the pertinent solids reactions involving calcium compounds are given in Table C-7. Mean heat capacities above 60°F are shown in Table C-8. Heats of formation and heats of reaction are shown in Table C-9.

Plots of the equilibrium constants versus temperature for reactions involving CaS are shown in Figures C-2 and C-3.

TABLE C-I

Effect of Temperature and Sulfur Partial Pressure on Distribution of Sulfur Species

Mol Fraction S_8	Mol Fraction S_6	Mol Fraction S_2	Partial Pressure of Total Sulfur, atm	Atoms Sulfur/Mol Total Sulfur
			250°F	
.8575	.1424	.0001	4.85×10^{-5}	7.714
.8472	.1527	.0001	3.54×10^{-5}	7.694
.8080	.1917	.0003	1.24×10^{-5}	7.615
.7567	.2426	.0007	$.396 \times 10^{-5}$	7.511
.7022	.2963	.0015	$.142 \times 10^{-5}$	7.398
			300°F	
.8249	.1749	.0002	2.33×10^{-4}	7.649
.8000	.1997	.0003	1.25×10^{-4}	7.599
.7473	.2520	.0007	$.401 \times 10^{-4}$	7.492
.6916	.3068	.0016	$.144 \times 10^{-4}$	7.377
.6230	.3735	.0035	$.0482 \times 10^{-4}$	7.232
			400°F	
.7566	.2428	.0006	3.11×10^{-3}	7.511
.7158	.2831	.0011	1.40×10^{-3}	7.427
.6501	.3474	.0025	$.481 \times 10^{-3}$	7.290
.5841	.4108	.0051	$.171 \times 10^{-3}$	7.148
.5072	.4819	.0109	$.0592 \times 10^{-3}$	6.971
			500°F	
.6903	.3080	.0017	2.42×10^{-2}	7.374
.5903	.4045	.0052	$.508 \times 10^{-2}$	7.160
.5204	.4693	.0103	$.192 \times 10^{-2}$	6.999
.4410	.5374	.0216	$.0680 \times 10^{-2}$	6.795
.3682	.5906	.0412	$.0272 \times 10^{-2}$	6.572
			600°F	
.6079	.3873	.0048	9.81×10^{-2}	7.196
.5651	.4274	.0075	5.31×10^{-2}	7.100
.4937	.4913	.0150	2.02×10^{-2}	6.927
.4133	.5558	.0309	$.726 \times 10^{-2}$	6.703
.3401	.6019	.0580	$.294 \times 10^{-2}$	6.448
.2623	.6273	.1104	$.114 \times 10^{-2}$	6.083
.1958	.6163	.1879	$.0511 \times 10^{-2}$	5.640
			700°F	
.4614	.5159	.0227	.1300	6.832
.4146	.5512	.0342	.0724	6.692
.3404	.5955	.0641	.0294	6.424
.2612	.6175	.1213	.0115	6.037
.1934	.6018	.2048	.00517	5.568
.1279	.5380	.3341	.00234	4.919
.0801	.4431	.4768	.00124	4.253
			800°F	
.3287	.5949	.0764	.1825	6.352
.2822	.6075	.1103	.1063	6.123
.2117	.5997	.1886	.0472	5.669
.1423	.5448	.3129	.0211	5.033
.0910	.4582	.4508	.0110	4.378
.0499	.3398	.6103	.00601	3.658
.0264	.2368	.7368	.00378	3.106
			900°F	
.2170	.5970	.1860	.2764	5.690
.1751	.5726	.2523	.1714	5.341
.1164	.5012	.3824	.0859	4.703
.0670	.3899	.5431	.0448	3.962
.0369	.2822	.6809	.0271	3.350
.0176	.1817	.8007	.0171	2.832
.0084	.1149	.8767	.0118	2.510
.0016	.0398	.9586	.00609	2.169
			1000°F	
.0977	.4625	.4398	.3071	4.436
.0572	.3561	.5867	.1749	3.768
.0288	.2423	.7289	.1042	3.142
.0143	.1588	.8269	.0698	2.721
.0063	.0946	.8991	.0475	2.416
.0029	.0571	.9400	.0345	2.246
.0005	.0189	.9806	.0186	2.078
			1200°F	
.0055	.0870	.9075	.546	2.381
.0025	.0523	.9452	.398	2.224
.0010	.0294	.9696	.287	2.124
.0004	.0172	.9824	.216	2.072
.0001	.0055	.9944	.120	2.022
.0000	.0007	.9993	.0328	2.003

TABLE C-2

Equilibrium Constants for Gas Reactions

Temperature in °Kelvin

$$\ln K = A + BT + CT^2 + D/T$$

	A	B	C x 10^6	D	Temperature Range, °K
K1 $CO + 1/2\ S_2 = COS$	-15.5992	.0122924	-8.01042	12,017.2	300-900
	-10.3503	.0006332	-.10012	11,327.0	900-1400
K2 $H_2 + 1/2\ S_2 = H_2S$	-3.3749	-.0027184	1.01362	10,039.6	300-900
	-4.9853	-.0007315	.18766	10,480.5	900-1400
K3 $2H_2 + SO_2 = 1/2\ S_2 + 2H_2O$	-4.8008	.0035970	-2.26137	15,353.9	300-900
	-1.4871	-.0021610	.43958	14,786.0	900-1400
K4 $2CO + SO_2 = 1/2\ S_2 + 2CO_2$	-15.7562	.0052624	-2.65427	25,277.0	300-900
	-14.3343	.0015907	-.35856	25,314.0	900-1400
K6 $3S_8 = 4S_6$	21.9713	-.003582	3.5055	-15,135.4	300-800
K8 $S_8 = 4S_2$	-33.2782	.132324	-63.9707	-29,596.0	300-800
K5 $2H_2S + SO_2 = 3/2\ S_2 + 2H_2O$	1.99482	.0089502	-4.6424	-4370.84	300-900
K7 $H_2O + CO = H_2 + CO_2$	-6.21477	.0016890	-.34401	5,187.25	900-1400
K9 $CO + 3H_2 = CH_4 + H_2O$	-33.415	.0030594	-1.03191	28,104	900-1300

TABLE C-3

Numerical Values of Equilibrium Constants for Table C-2

Temperature in °F

°F	K1	K2	K3	K4	K6	K8	K5	K7	K9
200	1.05×10^{8}	1.55×10^{9}	1.80×10^{15}	5.27×10^{21}	3.17×10^{-8}	2.03×10^{-29}	.000749		
300	1.66×10^{7}	2.76×10^{8}	1.45×10^{14}	8.45×10^{19}	3.88×10^{-7}	2.61×10^{-26}	.00190		
400	8.04×10^{5}	1.57×10^{7}	2.26×10^{12}	9.35×10^{16}	2.44×10^{-5}	5.75×10^{-21}	.00914		
500	73,900	1.60×10^{6}	8.36×10^{10}	4.35×10^{14}	6.62×10^{-4}	1.56×10^{-16}	.0325	-	
600	10,600	2.49×10^{5}	5.72×10^{9}	5.62×10^{12}	9.81×10^{-3}	8.48×10^{-13}	.0925	-	
700	2,090	5.27×10^{4}	6.15×10^{8}	1.55×10^{11}	.0937	1.26×10^{-9}	.221	-	
800	505	1.42×10^{4}	9.29×10^{7}	7.55×10^{9}	.644	6.30×10^{-7}	.461	-	
900	158	4,620	1.82×10^{7}	5.73×10^{8}	3.43	1.25×10^{-4}	.856	-	-
1000	58.1	1,750	4.39×10^{6}	6.16×10^{7}	15.1	.0108	1.44	-	-
1200	11.4	353	4.01×10^{5}	1.55×10^{6}	188	9.54	3.22	1.965	6.97×10^{-2}
1400	3.18	99.6	6.35×10^{4}	9.15×10^{4}	--		6.39	1.20	1.569×10^{-2}
1600	1.15	35.9	1.38×10^{4}	9,280	--		10.7	.819	1.224×10^{-3}
1800	.501	15.5	3,900	1,420	--		16.3	.603	1.486×10^{-4}
2000	.251	7.64	1,340	296	--		22.9	.471	-

TABLE C-4

Heat Capacities at Zero Pressure

Temperature in °Kelvin

$$Cp = A + BT + CT^2 + DT^3 + E/T^2$$

	A	B	C x 10^6	D x 10^9	E	Temp. Range, °K
S_8	28.51	.03771	-25.25			300-800
S_6	23.13	.01852	-3.137			300-1000
S_2	8.633	.000272			-87,826	300-1400
COS	9.678	.005978	-.1903		-123,658	↓
H_2S	7.344	.001851	3.364	-1.623		↓
SO_2	5.855	.01534	-11.002	2.842		↓
N_2	7.098	-.001431	3.490	-1.348		↓
CO	5.551	.003185	-.8609		48,814	↓
CO_2	5.101	.015568	-10.238	2.552		↓
H_2	7.219	-.000674	.6840		-16,003	↓
$H_2O_{(g)}$	7.757	.0000003	3.219	-1.125		↓
CH_4	1.3609	.021486	-5.80317		112,176	↓
O_2	6.055	.0036021	-1.6265	.2825		↓
Air	5.8254	.002572	-.52567		36,576	300-1000

TABLE C-5

Mean Heat Capacities Above 60°F, Gases

Temperatures in °F

$$\bar{C}p = A + BT + CT^2 + DT^3$$

Btu/Lb Mol/°F

	A	B	C x 10^6	D x 10^9	Temp. Range, °F
S_8	36.903	.006734	-2.598		60-1000
S_6	27.940	.004678	-.321		60-1300
S_2	7.680	.001251	-.640	.126	60-2000
COS	9.718	.003033	-1.096	.177	↓
H_2S	8.065	.000916	.214	-.070	
SO_2	9.274	.002798	-.898	.121	
N_2	6.941	.000037	.252	-.058	
CO	6.925	.000105	.266	-.070	
CO_2	8.632	.002958	-.844	.109	
H_2	6.910	.000135	-.044	.022	
$H_2O_{(g)}$	7.974	.000410	.239	-.048	
CH_4	8.1915	.0033201	.4754	-.2312	
O_2	6.9211	.00077623	-.1442	.012092	
Air	6.953	-.000003471	.3839	-.1108	60-1340

Heat content of steam (1 atm) above liquid water at 60°F.

Btu/Lb = $1021.08 + .48540T - 35.83 \times 10^{-6}\ T^2 + 34.46 \times 10^{-9}\ T^3$ 220-1000
Btu/Lb = $1039.25 + .41916T + 46.60 \times 10^{-6}\ T^2$ 1000-1600*

* Can be extrapolated accurately to 2000°F.

TABLE C-6

Heats of Formation at 25°C, Gases

cal/g mol

	ΔHf
$S_8(g)$	+24,200
$S_6(g)$	+25,580
$S_2(g)$	+30,840
COS	-33,080
H_2S	-4,880
SO_2	-70,960
CO	-26,416
CO_2	-94,052
$H_2O_{(g)}$	-57,798
$H_2O_{(1)}$	-68,430
CH_4	-17,889

Heats of Reaction at 25°C, Gas Reactions

cal/g mol

Reaction		
1	$CO + 1/2\ S_2 = COS$	-22,080
2	$H_2 + 1/2\ S_2 = H_2S$	-20,300
3	$2H_2 + SO_2 = 1/2\ S_2 + 2H_2O_{(g)}$	-29,220
4	$2CO + SO_2 = 1/2\ S_2 + 2CO_2$	-48,890
5	$2H_2S + SO_2 = 3/2\ S_2 + 2H_2O_{(g)}$	+11,380
6	$3S_8 + 4S_6$	+29,720
8	$S_8 = 4S_2$	+99,160
6a	$1/6\ S_6 = 1/2\ S_2$	+11,160
8a	$1/8\ S_8 = 1/2\ S_2$	+12,400
5a	$2H_2S + SO_2 = 1/2\ S_6 + 2H_2O_{(g)}$	-22,090
5b	$2H_2S + SO_2 = 3/8\ S_8 + 2H_2O_{(g)}$	-25,800

Heat of Vaporization of Sulfur

Temperature in °F

$$\text{Btu/Lb} = 211.1 - .3302T + 434.6 \times 10^{-6}\ T^2 - 214.4 \times 10^{-9}\ T^3$$

TABLE C-7

Equilibrium Constants for Solids Reactions

Temperature in °Farenheit

$\ln K = A + BT + CT^2 + D/T$

		A	B	$C \times 10^6$	D	Temperature Range, °F
K10	$3/4\ CaSO_4 + 1/4\ CaS = CaO + SO_2$	71.5076	-.031250	5.79655	-67,104	1500-2000
K11	$1/4\ CaSO_4 + CO = 1/4\ CaS + CO_2$	3.0040	-.000751	.01932	4, 232	1500-2000
K12	$CaO + H_2S = CaS + H_2O$	17.5646	-.0092926	1.7716	-1,070	1300-2000
K13	$CaO + 3/4\ S_2 = CaS + 1/2\ SO_2$	-7.22273	.0025330	-.36880	15,200	1500-2000
K14	$CaSO_4 + S_2 = CaS + 2\ SO_2$	-6.55015	.0118713	-1.86265	-12,576	1500-2000
K15	$CaCO_3 = CaO + CO_2$	-.840165	.0074015	-1.28243	-12,932	all
K16	$CaCO_3 + H_2S = CaS + CO_2 + H_2O$	16.6700	-.0018535	.480912	-13,977.2	1100-2000

TABLE C-8

Mean Heat Capacities Above 60°F, Solids

Temperature in °Farenheit

$$\bar{C}p = A + BT + CT^2$$

Btu/lb Mol/°F

	A	B	$C \times 10^6$	Temperature Range, °F
$CaSO_4$	23.57	.00645	-.0383	60-2000
CaS	10.14	.00230	-.502	↓
CaO	10.98	.00071	-.0772	
MgO	9.77	.00081	-.0387	
MgO·CaO	20.75	.00152	-.116	
$MgO \cdot CaCO_3$	30.64	.00506	-.193	
Char Carbon	1.447	.00291	-.643	
MgO·CaS	19.91	.00311	-.541	(30,31)
		Btu/lb/°F		
Ash*	.207	.000029	-.0034	60-2000(31)
		Heat Content Above 60°F Btu/lb		
Coal**	-12.2	.1879	.00025	60-800

* Also used for impurity content of acceptor.

** Including products of pyrolysis.

TABLE C-9

Heats of Formation at 25°C, Solids

cal/g mol

	ΔH_f
$CaSO_4$	-344,090
CaS	-113,550
$CaCO_3$	-288,280
CaO	-151,900

Heats of Reaction at 25°C, Solids Reactions

cal/g mol

$3/4\ CaSO_4 + 1/4\ CaS = CaO + SO_2$	+63,600
$1/4\ CaSO_4 + CO = 1/4\ CaS + CO_2$	-10,002
$CaO + H_2S = CaS + H_2O_{(g)}$	-14,570
$CaO + 3/4\ S_2 = CaS + 1/2\ SO_2$	-20,260
$CaSO_4 + S_2 = CaS + 2\ SO_2$	+57,780
$CaCO_3 = CaO + CO_2$	+42,330
$CaCO_3 + H_2S = CaS + CO_2 + H_2O_{(g)}$	+27,760
$CaS + 3/2\ O_2 = CaO + SO_2$	-109,310
$CaS + 2\ O_2 = CaSO_4$	-230,540

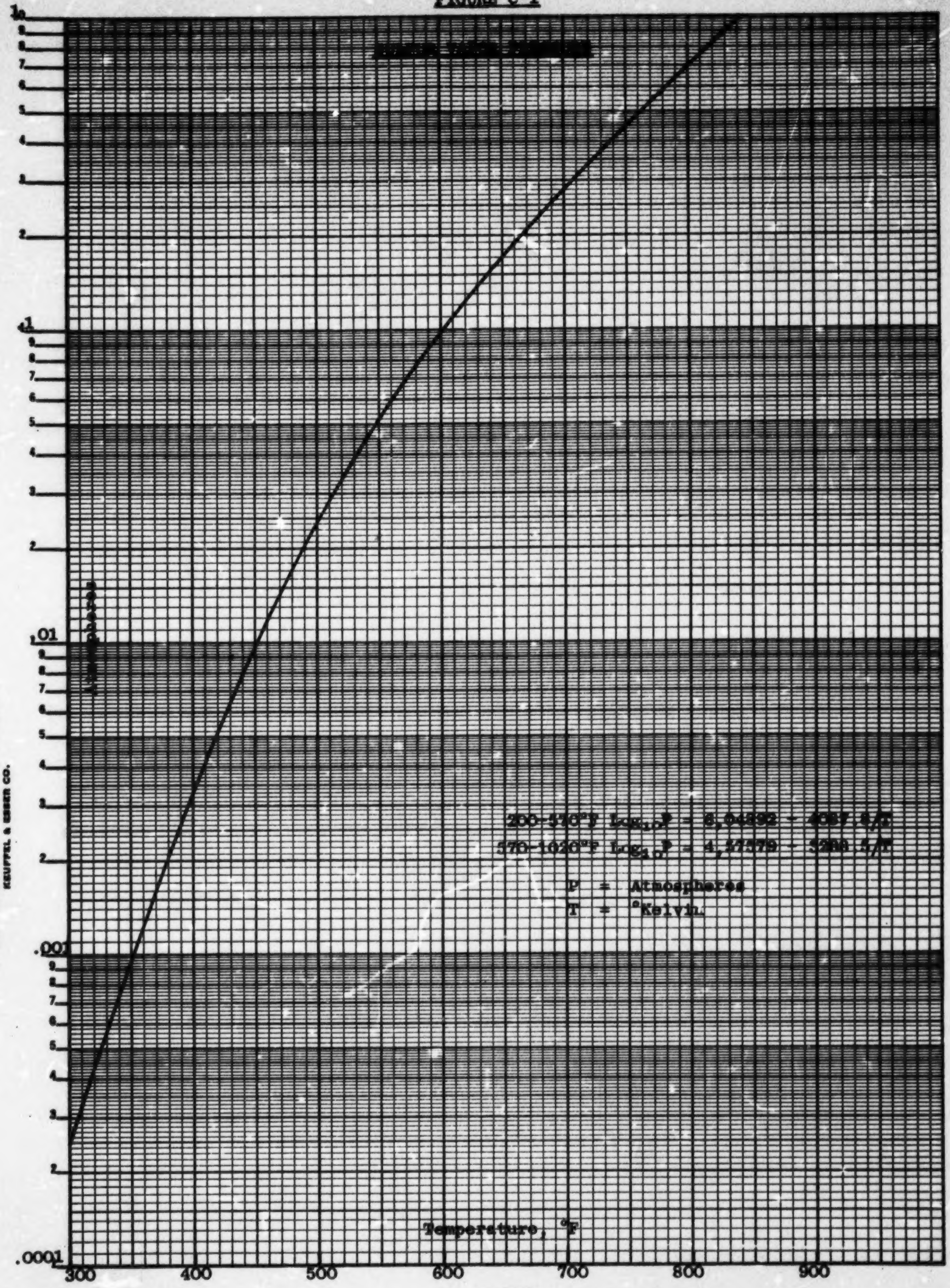
Heat of Combustion

Btu/lb mol

Char Carbon	178,540-4T*	(32)

* T is maximum temperature to which the char has been exposed, °Farenheit.

FIGURE C-1



200-570°F $\text{Log}_{10}P = 6{,}04892 - 4067.8/T$

570-1020°F $\text{Log}_{10}P = 4{,}37579 - 5288.5/T$

P = Atmospheres

T = °Kelvin

K+E SEMI-LOGARITHMIC 46 6013
4 CYCLES X 70 DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.

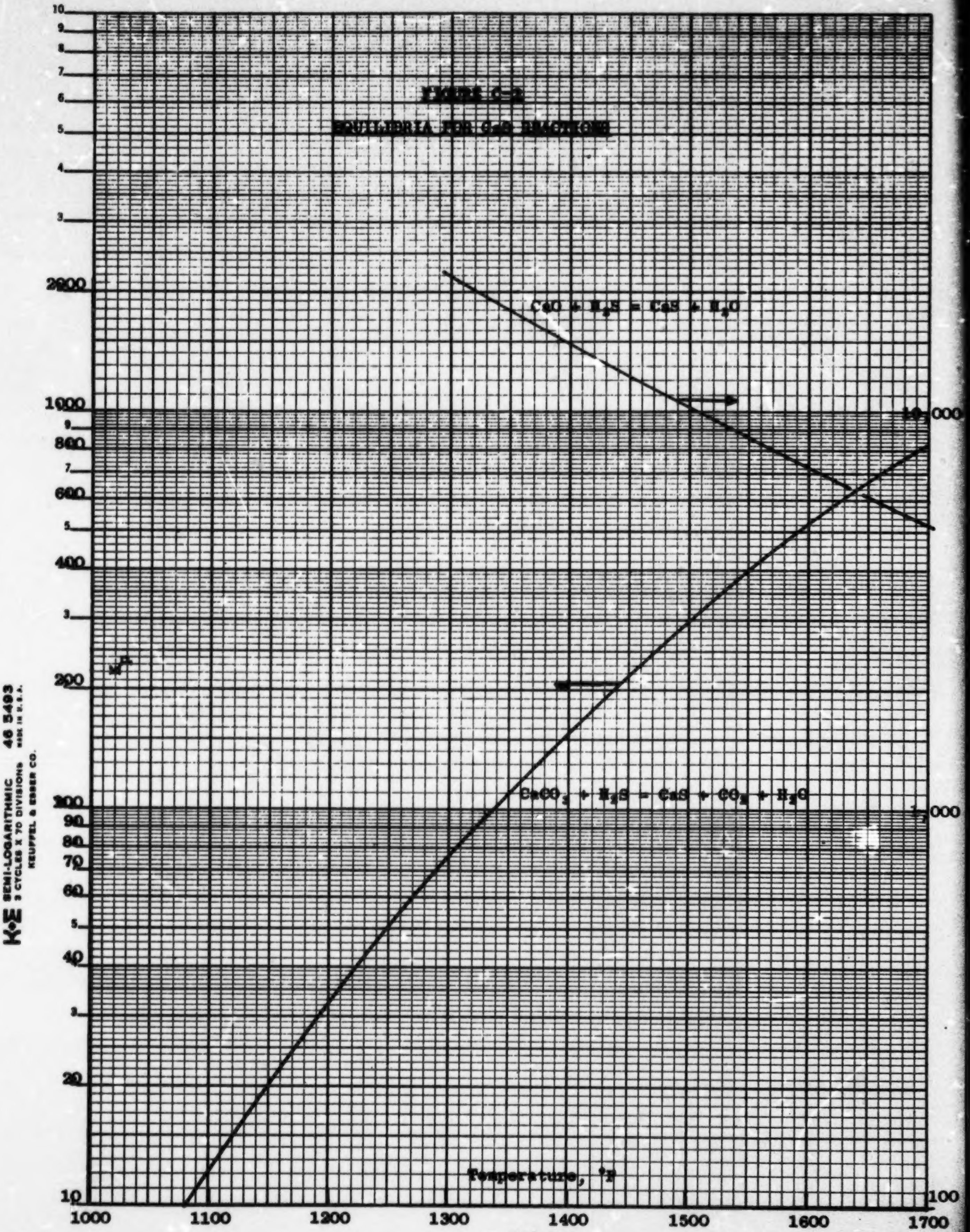


FIGURE C-2

EQUILIBRIA FOR CaO REACTIONS

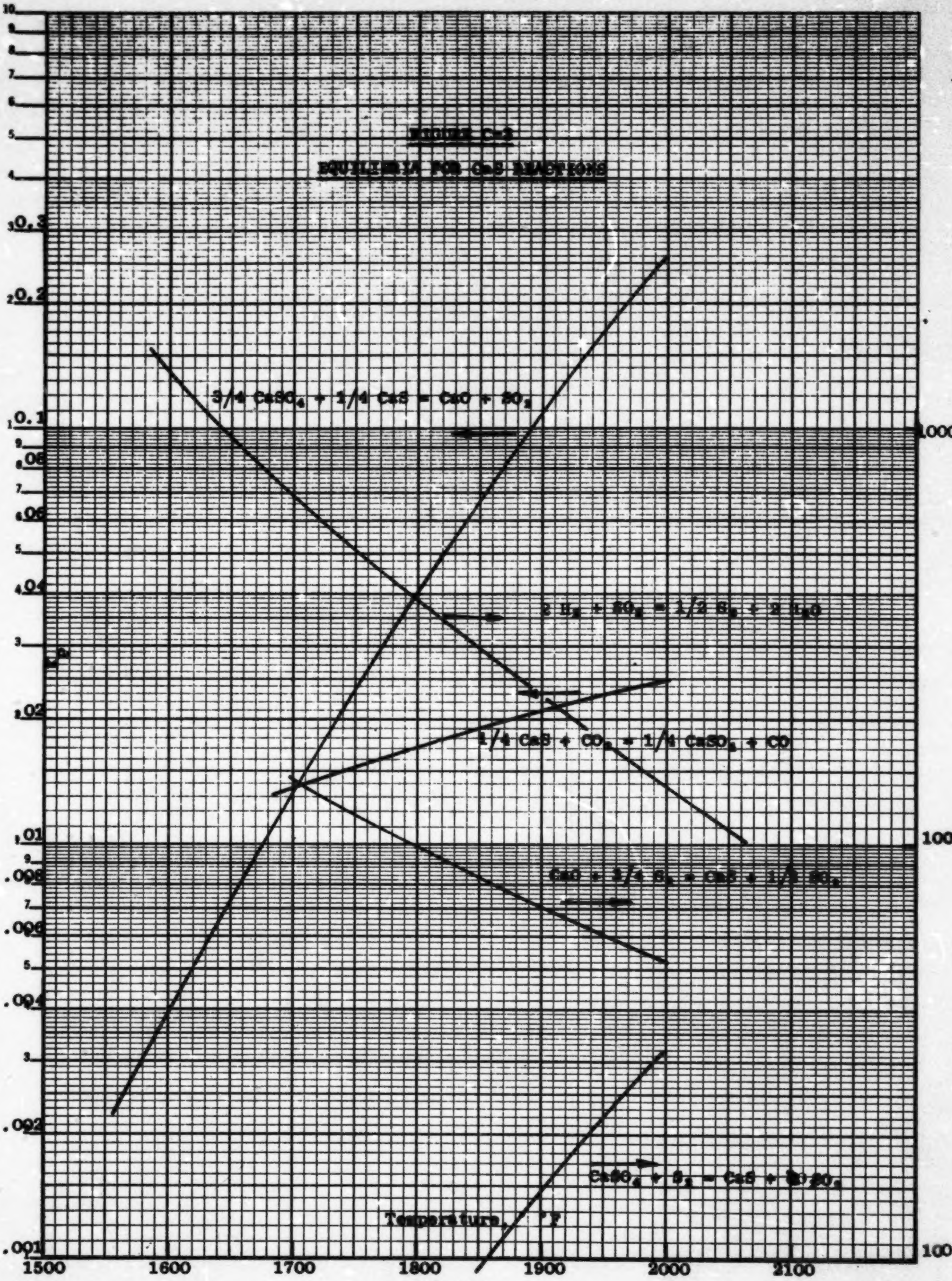


FIGURE C-2

EQUILIBRIA FOR CaS REACTIONS

3 CYCLES X 70 DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.

APPENDIX D

Modified Sulfur Recovery System

Introduction and Summary

It would be desirable to produce directly in the regeneration of sulfided lime acceptor a feed suitable in composition to conduct a liquid-phase Claus reaction, i.e., one containing a ratio of H_2S/SO_2 of 2. Perhaps the most straightforward method of doing this would be to inject oxygen into the offgases from the Squires reactor. Air cannot be used since it introduces nitrogen as a diluent which would accumulate in the recycle system. The system investigated here utilizes $CaSO_4$ as an oxidizing agent or oxygen carrier.

Two systems were evaluated here, namely, the single and two-stage processes. The first appears to be impractical while the second seems to have merit.

The single-stage operation at 15-20 atmospheres, requires an operating temperature above 1400°F to achieve the desired result of H_2S/SO_2 ratio = 2. Under these conditions, however, the total "atomic" percent of sulfur in the product gas is limited to a maximum value of about 1 to 1.25%. The "optimum" temperature at this pressure level is about 1600°F. The optimum temperature as well as the sulfur concentration in the offgas increases with increasing pressure.

A more practical system involves use of a two-stage process where the CaS-$CaCO_3$ couple, i.e., the "Squires" reaction is carried out at a lower temperature and the product gas is oxidized to produce Claus feed via the CaS-$CaSO_4$ couple. In this case, the temperature and pressure at which the Squires reaction is conducted determine the sulfur concentration in the product gas. The second or oxidation stage must now be carried out at a higher temperature to achieve the desired H_2S/SO_2 ratio. The minimum temperature for the second stage increases with increasing steam pressure and is 1600°F for a steam pressure of 6.4 atmospheres.

Another alternative is to condense steam out of a fraction of the Squires product gas (at least 1/3 of the gas) and oxidize this fraction by means of the CaS-$CaSO_4$ couple to produce a gas containing a low H_2S/SO_2 ratio. This gas would then be blended with the untreated gas to produce a Claus feed.

Discussion

Single-Stage Operation

The thermodynamic performance is determined by establishment of equilibrium simultaneously in the reactions below:

$$CO_2 + 3/4\ CaSO_4 + 1/4\ CaS = CaCO_3 + SO_2 \qquad K_1 \qquad (1)$$

$$CO_2 + 1/4\ CaSO_4 + 3/4\ CaS = CaCO_3 + 1/2\ S_2 \qquad K_2 \qquad (2)$$

$$4/3\ H_2S + 2/3\ SO_2 = S_2 + 4/3\ H_2O \qquad K_3 \qquad (3)$$

Establishment of equilibrium in the above reactions automatically insures that equilibrium will be maintained also in the "Squires" reaction, i.e.,

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S \qquad (4)$$

The net reaction neglecting the relatively small amount of elemental sulfur produced is:

$$3/2\ CaS + 1/2\ CaSO_4 + 4/3\ H_2O + 2\ CO_2 = 2\ CaCO_3 + 4/3\ H_2S + 2/3\ SO_2 \qquad (4a)$$

It is assumed that part of the CaS in the acceptor will be oxidized to $CaSO_4$ by air in a transfer line reactor in which the acceptor is passed from the sulfur removal step to the acceptor regeneration step. It also is assumed that a sufficiently high partial pressure of CO_2 will be maintained to prevent calcination of the acceptor.

A restraint that is put on the system is that the product be a suitable feed to a Claus unit, i.e., the ratio $P_{H_2S}/P_{SO_2} \cong 2$. With this restraint it is easy to show that the partial pressure of steam is given by the relationship:

$$P_{H_2O} = 2\left(K_3\right)^{3/4}\left(\frac{K_1}{K_2}\right)^{3/2}$$

i.e., the steam partial pressure at equilibrium is independent of the applied CO_2 pressure. The H_2S, SO_2 and S_2 partial pressures are given by:

$$P_{SO_2} = K_1\ P_{CO_2}$$

$$P_{S_2} = (K_2)^2\left(P_{CO_2}\right)^2$$

$$P_{H_2S} = 2\ P_{SO_2} = 2\ K_1\ P_{CO_2}$$

The results of the equilibrium calculations at two total pressure levels of 15 and 20 atmospheres, respectively, are given in Table D-1. It is noted that the maximum total "atomic" percent sulfur is very low, i.e., 1.1% at 1600°F and 15 atmospheres and 1.28% at 1625°F and 20 atmospheres. The equilibrium sulfur concentration goes up slowly with pressure and still amounts to only 2.05% at 1710°F and 50 atmospheres. It is concluded that the single-stage regeneration procedure is impractical.

Two-Stage Process

The flow sheet of the two-stage process is given in Figure D-1. The H_2S-CO_2-H_2O mixture leaving the "Squires" reactor at about 1300°F is oxidized at a higher temperature by $CaSO_4$ to generate a Claus feed via the reactions:

$$1/2\ CaSO_4 + 2\ H_2S = 1/2\ CaS + S_2 + 2\ H_2O \qquad K_4 \qquad (4)$$

$$S_2 + 4/3\ H_2O = 4/3\ H_2S + 2/3\ SO_2 \qquad 1/K_3 \qquad (3)$$

Net Reaction,

$$1/2\ CaSO_4 + 2/3\ H_2S = 1/2\ CaS + 2/3\ SO_2 + 2/3\ H_2O \qquad K_5 = K_4/K_3 \qquad (5)$$

Conditions must be chosen such that the net product from the $CaSO_4$ reactor has the proper H_2S/SO_2 ratio = 2 for the subsequent liquid-phase Claus reaction.

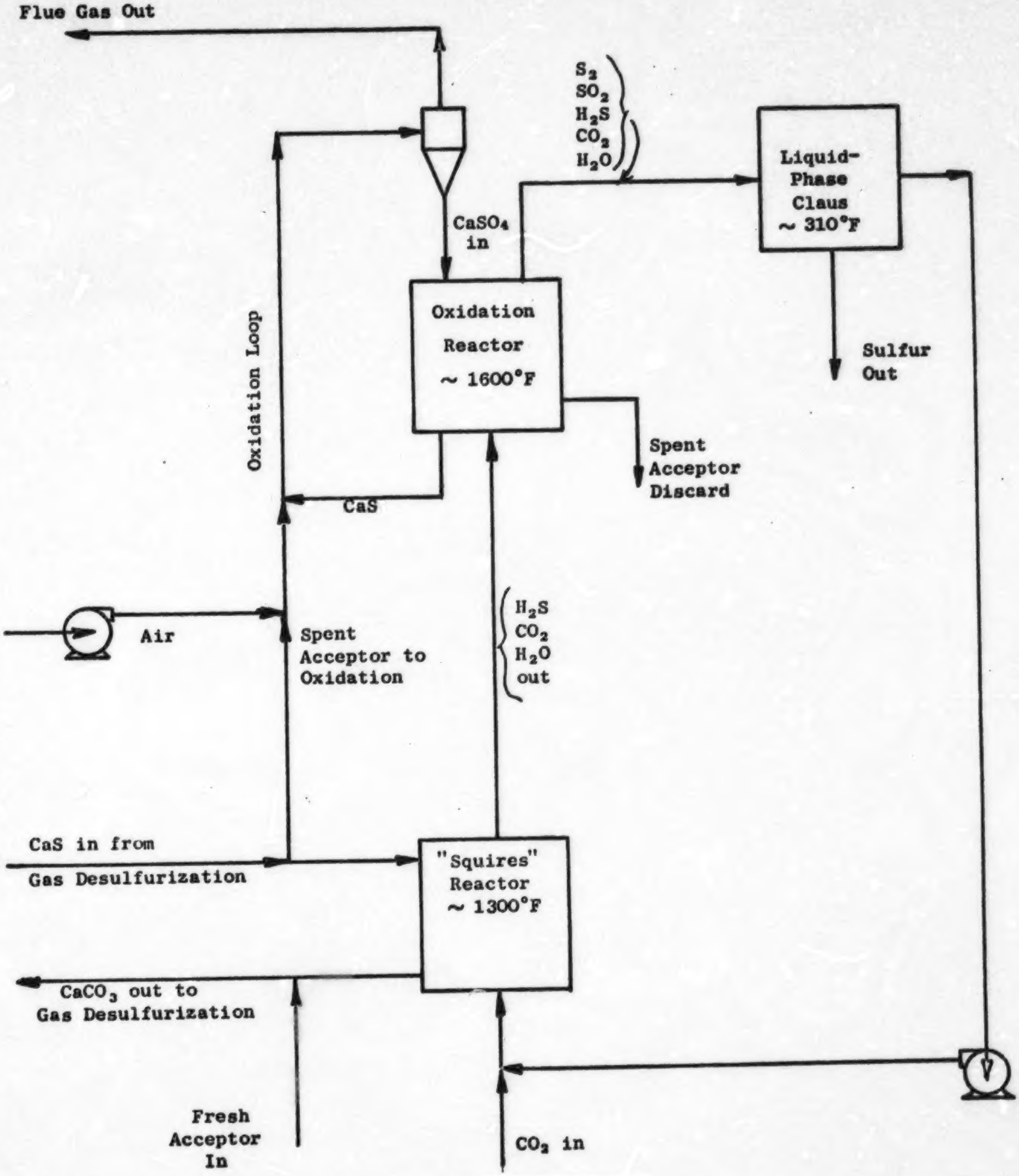
Table D-1

Thermodynamic Equilibria in the $CaS-CaSO_4-CaCO_3-CO_2-H_2O-H_2S-SO_2-S_2$ System

Temperature, °F	1390	1540	1600	1625	1710	1710
K_1	.0017	.0039	.0053	.0059	.0089	→
K_2	.0088	.0073	.0068	0.0665	.0062	→
K_3	3.75	5.10	5.63	5.85	6.78	→
$K_3 \left(\frac{K_1}{K_2}\right)^2$	0.140	1.45	3.40	4.62	13.98	→
Pressures, Atm.						
P_{H_2O}	0.46	2.64	5.02	6.28	14.45	→
P_{CO_2}	14.4	12.2	9.80	8.55	0.50	35.0
P_{SO_2}	0.0245	0.0475	0.052	0.0505	0.0045	0.312
P_{H_2S}	0.049	0.095	0.104	0.1010	0.0089	0.624
P_{S_2}	0.016	0.008	0.0045	0.0035	0.0000	0.047
Total	14.93	15.00	15.00	14.98	14.96	50.3
Atom, % S	0.71	1.06	1.10	1.06	0.09	2.05
P_{H_2O}	0.46	2.64	5.02	6.28	14.45	
P_{CO_2}	19.4	17.1	14.7	13.5	5.45	
P_{SO_2}	0.033	0.067	0.078	0.080	0.049	
P_{H_2S}	0.066	0.134	0.156	0.160	0.097	
P_{S_2}	0.029	0.016	0.010	0.008	0.002	
π	20.00	19.95	19.96	20.03	20.05	
Atom, % S	0.785	1.17	1.27	1.28	0.75	

FIGURE D-1

Modified Sulfur Recovery Section


Flue Gas Out
S_2
SO_2
H_2S
CO_2
H_2O
Liquid-Phase Claus ~ 310°F
$CaSO_4$ in
Oxidation Reactor ~ 1600°F
Sulfur Out
Oxidation Loop
Spent Acceptor Discard
CaS
Air
Spent Acceptor to Oxidation
H_2S
CO_2
H_2O
out
CaS in from Gas Desulfurization
"Squires" Reactor ~ 1300°F
$CaCO_3$ out to Gas Desulfurization
Fresh Acceptor In
CO_2 in

Now, if equilibrium is established in the $CaSO_4$ reactor, we have:

$$\left(P_{H_2O}\right)^{2/3} \Big/ \left(\frac{P_{H_2S}}{P_{SO_2}}\right)^{2/3} = K_5 = K_4/K_3$$

But, since $P_{H_2S}/P_{SO_2} = 2$, the above relationship can be used to define the temperature at which the reaction must be carried out, consistent with the partial pressure of steam.

A typical calculation is given in Table D-3 for operation of the "Squires" reaction at 1300°F, with 80% approach to equilibrium, and a total pressure of 15 atmospheres.

It is noted that a suitable operating temperature for the oxidation reactor is about 1600°F. The heat required to raise the temperature to 1600°F is "automatically" supplied by the heat of oxidation, i.e., by reaction (6) below:

$$1/2\ CaS + O_2 = 1/2\ CaSO_4 \qquad (6)$$

which combined with reaction (5) gives the overall reaction where 1/3 of the H_2S is oxidized to SO_2 via reaction (5),

$$2/3\ H_2S + O_2 = 2/3\ SO_2 + 2/3\ H_2O \quad \Delta H \cong 161{,}000 \text{ Btu/mol} \qquad (7)$$

Another alternative is to condense the steam out of 1/3 or more of the gas and oxidize it more completely to SO_2 while the remainder of the gas is by-passed around the oxidation reactor.

The use of other oxygen carriers than the CaS-$CaSO_4$ couple may be considered to avoid the cost of an oxygen plant. However, the above couple appears to be the most "natural" to use in the present context.

Perhaps a more "natural" application of the system would be to the regeneration of $CaSO_4$ produced in a fluid bed boiler. The cycle in this case would comprise: 1) partial reduction with coal or a reducing gas to produce a CaS-$CaSO_4$ mixture, and 2) the product from step (1) would then be passed in series through the oxidation and "Squires" reactors of Figure D-1. The $CaCO_3$ product leaving the "Squires" reactor would be returned to the fluid bed boiler.

Table D-2

Equilibria in $CaSO_4$ Oxidation of Squires Product Gas

Temperature, °F	1400	1500	1600
K_4	2.16	5.43	12.28
$1/K_3$	0.262	0.212	0.178
$K_5 = K_4/K_3$	0.565	1.16	2.18
Equilibrium P_{H_2O} atm If $P_{H_2S/SO_2} = 2.0$	0.85	2.5	6.45

Table D-3

Composition of Feed and Product

	Squires Reaction Product at 1300°F		After $CaSO_4$ Oxidation at 1600°F	
	Partial Pressure, Atm.	Mol %	Partial Pressure, Atm.	Mol %
H_2O	6.35	42.4	6.453	43.23
CO_2	8.10	54.2	8.000	53.62
H_2S	0.51	3.4	0.297	1.98
SO_2	--		0.149	0.99
S_2	--		0.027	0.18
Total	14.96	100.0	14.926	100.00

APPENDIX E

Conversion Factors - English to Metric Units

	English System	Metric Equivalent
Length	inch	2.54 centimeter
	foot	0.305 meter
Area	square foot	0.093 square meter
Volume	gallon	3.785 liter
	cubic foot	28.32 liters
Mass	pound	453.6 grams
Pressure	pound per square inch	51.70 millimeters Hg
	atmosphere	760 millimeters Hg
Temperature	° Fahrenheit	1.8 (°Celsius) + 32
Energy	Btu	1055 joules
	horsepower hour	2.69 x 10^6 joules